Temperature Dependences of Limiting Activity Coefficients and Henry's Law Constants for Nitrobenzene, Aniline, and Cyclohexylamine in Water

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Recommended data for the limiting activity coefficients (γ_1^∞) of nitrobenzene, aniline, and cyclohexylamine in water were established as a function of temperature by the simultaneous correlation of the values resulting from specialized vapor−liquid equilibrium measurements and related thermal data for highly dilute solutions. The new values of γ_1^∞ were determined by the Rayleigh distillation, circulation still, and headspace analysis methods. The limiting partial molar excess heat capacities were derived from measurements by the Picker flow microcalorimetry. These values were combined with all available literature data on the limiting activity coefficients and the limiting partial molar excess enthalpies. This allowed us to produce a thermodynamically consistent fit of γ_1^∞ between 273 K and 373 K, which was in turn used in combination with pure solute vapor pressures to calculate the Henry's law constants (k_H).

Introduction

Nitrobenzene, aniline, and cyclohexylamine are important chemical intermediates produced worldwide on a large scale and further extensively used in industry to manufacture rubber, agrochemicals, dyes and pigments, pharmaceuticals, and synthetic fibers. In many of these processes, including the production of these three chemicals themselves, large quantities of water are involved, adequate separation of the dissolved organics from water requiring great effort and cost. As nitrobenzene, aniline, and cyclohexylamine are hazardous materials that often appear on priority pollutant lists,[1] increasingly strict environmental protection regulations give an additional strong impetus for improvement of their respective separation processes. To abate pollution of wastewater effluents and optimize separation costs, reliable data on fluid phase equilibria in highly dilute aqueous solutions of these substances are needed over an extended environmental range of temperatures. Existing data are, however, insufficient, their fragmentary character hampering conclusive mutual comparisons.

With the aim to meet the indicated data needs, we have established recommended thermodynamically consistent temperature dependences of the limiting activity coefficients (γ_1^∞) of nitrobenzene, aniline, and cyclohexylamine in water, which are reliable in the temperature range of environmental and industrial interest: (273 to 373) K. To that end, we employed phase equilibrium data together with calorimetric data on infinite dilution partial molar excess enthalpies $\bar{H}_1^{\mathrm{E},\infty}$ and heat capacities $\bar{C}_{p,1}^{\mathrm{E},\infty}$, combining results measured in this work with those from literature. This strategy,[2] helpful to overcome limitations of individual experimental methods, has proven to be highly efficient for establishing the $\gamma_1^\infty(T)$ dependence, which for liquid organic solutes in water is typically nonmonotonic, with a maximum in the temperature region of interest. Analogous recommendations were further inferred for the temperature dependences of the Henry's law constants.

Experimental Section

Materials. Organic compounds used as solutes were all obtained as special grade purity chemicals from the Moravian Chemical Works (Ostrava, Czech Republic). Their declared purity (> 99.9 %) was verified by gas chromatography using a DB-5 capillary column. Before the measurements, they were dried with 4A molecular sieves and stored in the dark. All samples were kept and manipulated under a protective nitrogen atmosphere. Water used as the solvent was distilled and subsequently treated by a Milli-Q Water Purification System (Millipore, USA). To remove possible traces of dissolved carbon dioxide, the water was either stripped by nitrogen (for VLE measurements) or was partially degassed by filtration under vacuum (for calorimetric measurements).

VLE Measurements. To determine the limiting activity coefficients, three experimental techniques were employed in this work: Rayleigh distillation method (RDIST),[3] method of the circulation still (CIRC),[4] and headspace analysis (HSA).[2] The techniques were applied alternatively, the choice being according to system characteristics and conditions, to achieve the best accuracy of the determinations.[5] The RDIST and CIRC methods were used at higher temperatures (RDIST from 333 K to 353 K and CIRC at near normal boiling temperatures of water) where system volatility conditions are well-suited for their application and pure solute vapor pressures are known with an uncertainty allowing reliable evaluation of γ_1^∞. At lower temperatures, where the vapor pressure values for the solutes examined are rather uncertain, the HSA method with calibration by the pure solute saturated vapor was used, as for this procedure no knowledge of the solute vapor pressure to determine γ_1^∞ is needed. In the treatment of all VLE data, the vapor phase was considered as ideal gas since our estimations showed vapor-phase nonideality corrections to be negligible as compared to experimental uncertainties.

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The methods used in this work have been described by us in detail previously,[2−4] and only a brief outline supplemented by some details specific to the present application is given below. For cyclohexylamine, a solute that undergoes appreciable hydrolysis, the calculation of γ_1^∞ from the present VLE measurements is more involved and is described below in a separate paragraph.

Rayleigh Distillation Method (RDIST). The RDIST technique is based on measuring the changes of the solution mass and the solute concentration resulting from a partial one-stage equilibrium distillation of a highly dilute solution ($x_1 < 10^{-3}$), which is accomplished by passing a slow stream of an inert gas (nitrogen) through the thermostated solution under study. From the RDIST measurement, γ_1^∞ is calculated by the following equation:

$$\gamma_1^\infty = \frac{p_2^{\mathrm{s}}}{p_1^{\mathrm{s}}}\left[1 + \frac{\ln(A_1/A_1^0)}{\ln(m/m^0)}\right] \tag{1}$$

where m and m^0 are the masses of the solution before and after the distillation, A_1^0 and A_1 are the proportional analytical responses to the solute concentrations in the original solution and in the remainder, and p_i^{s} is the pure component vapor pressure. With the nitrogen flow rates set between (4 and 12) mL·min^{-1} and the extent of distillation chosen according to the error analysis[3] to minimize the effect of analytical errors, the distillation experiments for the present systems took from (12 to 34) h, depending on the system and temperature. Samples of the original solution and of the distillation remainder were analyzed in this work either by UV spectroscopy (for nitrobenzene) or by gas chromatography (for aniline and cyclohexylamine). The spectroscopic analyses were carried out with a Varian spectrophotometer, model Cary 50 Bio. The UV absorbances were determined at the maximum absorbance wavelength in the differential mode against pure water using closed quartz cells of 10 mm optical length. The GC analyses were performed using an Agilent 6890 Plus gas chromatograph and a 0.5 m long stainless steel 1/8 in. o.d. column packed with Carbopack B coated with 4 % Carbowax 20M and 0.8 % KOH from Supelco. Samples were dosed by an Agilent 7683 automatic sampler, typically with dozen replicates each.

Circulation Still Method (CIRC). In this method, a VLE circulation still operated at constant pressure is employed to provide samples of the vapor and liquid in equilibrium in the region of high dilution; no measurement of temperature being needed as the boiling temperature of the solution is effectively the same as that of the neat solvent water. Provided the samples are analyzed by a method responding proportionally to the solute concentration, the value of γ_1^∞ is obtained from

$$\gamma_1^\infty = \frac{p_2^{\mathrm{s}}}{p_1^{\mathrm{s}}}\frac{A_1^{\mathrm{G}}}{A_1^{\mathrm{L}}} \tag{2}$$

where A_1^{G} and A_1^{L} are the responses for the samples of equilibrium vapor phase condensate and the corresponding liquid phase, respectively. Due to their rather poor boiling characteristics, the aqueous solutions studied in this work were boiled for extended periods of time (24 to 30) h to ensure the generation of truly representative equilibrium samples. UV spectrophotometry for aniline and nitrobenzene and gas chromatography for cyclohexylamine were used to analyze the obtained samples. The mole fractions of the solutions ranged from 10^{-6} to 10^{-5} for the UV and from 10^{-4} to 10^{-3} for the GC analysis. The analyses were carried out in the same manner as in the case of the RDIST method.

Table 1. Equilibrium Constants pK_b for Hydrolysis of Aniline and Cyclohexylamine and Equilibrium Constants pK_a, Standard Enthalpy $\Delta H_\mathrm{a}^\circ$, and Heat Capacity $\Delta C_{p,\mathrm{a}}^\circ$ Changes for the Dissociation of Corresponding Ammonium Ions at 298.15 K

	pK_b[a]	pK_a	$\Delta H_\mathrm{a}^\circ$ kJ·mol^{-1}	$\Delta C_{p,\mathrm{a}}^\circ$ J·K^{-1}·mol^{-1}
aniline	9.40	4.60[b]	31.09[b]	57[b]
cyclohexylamine	3.44	10.56[c]	59.66[c]	21[c]

[a] pK_b = pK_w − pK_a; pK_w = −408.174 + 15141.68/(T/K) − 0.09835(T/K) + 70.32965 ln(T/K).[6] [b] Ref 7. [c] Ref 8.

Headspace Analysis (HSA). The HSA method consists of a gas chromatographic determination of the equilibrium solute partial pressure above a highly dilute solution of known composition. Using the headspace above the pure liquid solute as a calibration standard and assuming the detector proportionality, the value of γ_1^∞ is obtained from

$$\gamma_1^\infty = \frac{A_1}{x_1 A_1^{\mathrm{s}}} \tag{3}$$

where A_1 and A_1^{s} are the headspace solute peak areas above a highly dilute solution with the solute mole fraction x_1 and above the pure liquid solute, respectively. In our apparatus,[2] the vapor phase is circulated by a chemically inert pump through the liquid phase in the equilibrium cell and the gas sampling loop of GC, which avoids perturbation of the equilibrium during sampling and suppresses sorption effects. For the present systems, the HSA measurements were carried out typically for five solution compositions in the range of solute mole fractions from 0.0001 to 0.0015, and the results were subsequently averaged or, when exhibiting a trend, extrapolated to infinite dilution.

Correction for Amine Hydrolysis. Amines are bases that in aqueous solutions hydrolyze according to

$$\mathrm{B} + \mathrm{H_2O} \rightleftarrows \mathrm{BH}^+ + \mathrm{OH}^- \tag{4}$$

which may appreciably affect thermodynamic behavior that these solutions exhibit at high dilutions. Hence, to properly treat the observed behavior of these solutions and, in particular, to evaluate true thermodynamic parameters corresponding to the neutral amine species, it is necessary to take into account the effect of the hydrolysis reaction. The equilibrium constants of amine hydrolysis K_b needed to establish the respective corrections can be obtained from more conventional dissociation constants K_a of respective ammonium ions and the ionic product of water K_w ($K_\mathrm{b} = K_\mathrm{w}/K_\mathrm{a}$). Values of these equilibrium constants at 298.15 K together with the standard dissociation enthalpies and heat capacities are listed in Table 1. Calculations based on these data indicate that while for aniline the degree of hydrolysis at conditions of our experiments is very small and the effect on the properties observed can be neglected, for cyclohexylamine, which is a much stronger base, the degree of hydrolysis is appreciable (from 0.06 to 0.16) and careful corrections are required. They were done as follows. The degree of hydrolysis ξ for a given total amine molality b_1 was calculated from

$$\xi = -K/2 - (K^2/4 + K)^{1/2} \tag{5}$$

where $K = K_\mathrm{b}/(b_1\gamma_\pm{}^2)$ and $\gamma_\pm$ is the mean activity coefficient estimated from the Debye−Hückel equation.

Considering that it is only the neutral amine species that undergoes the vapor−liquid partitioning, the following formulas

$$\gamma_1^\infty = \frac{p_2^s}{p_1^s}\frac{A_1^G}{A_1^L(1-\xi)} \tag{6}$$

and

$$\gamma_1^\infty = \frac{A_1}{x_1(1-\xi)A_1^s} \tag{7}$$

accounting for the amine hydrolysis were used to calculate γ_1^∞ from the CIRC and HSA measurements, respectively. Note that in contrast to eq 2, the application of eq 6 requires the composition of the equilibrium liquid phase to be known absolutely.

For RDIST method, the evaluation of γ_1^∞ accounting for the amine hydrolysis was more complicated. The following equation (for derivation see Appendix A):

$$\ln\frac{m}{m^0} - \int_{b_1^0}^{b_1}\frac{\mathrm{d}b_1}{b_1[\alpha_{12}^\infty(1-\xi)-1]} = 0 \tag{8}$$

where b_1^0 is the total solute molality in the original solution and b_1 is that in the remainder, was to be solved for the limiting relative volatility iteratively with the involved integral being evaluated numerically by the Simpson method. The first approximation of γ_1^∞ for the iterative procedure was conveniently obtained from eq 1.

Calorimetry. Concerning thermal properties, only heat capacity measurements were performed in this work, as reasonably accurate data on infinite dilution partial molar excess enthalpies $\bar{H}_1^{E,\infty}$ for the aqueous solutes studied are available in the literature. The heat capacities of dilute solutions were determined at 298.15 K using a Picker differential flow microcalorimeter (SETARAM, France).[9] The principle of the measurement is based on maintaining the thermal equilibrium between the measuring and reference cells, connected in series, through which previously thermostated water and dilute solutions are alternately pumped at the same flow rate. The relative difference of the electric power necessary to restore thermal balance after replacing water in the measuring cell by a solution is proportional to the relative difference of the heat capacities of the two liquids. The volumetric heat capacities are obtained with this technique. Densities of the solutions needed to convert these data to molar basis were measured by a vibrating platinum−thorium tube densimeter (type 03D, SODEV, Canada).[10]

The measurements were carried out for a series of a minimum six dilute solutions with the solute concentration varying in the range from (0.015 to 0.3) mol·kg^{-1} (for aniline and cyclohexylamine) or from (0.005 to 0.012) mol·kg^{-1} (for nitrobenzene). The limiting partial molar heat capacity $\bar{C}_{p,1}^\infty$ and volume $\bar{V}_1^\infty$ (although $\bar{V}_1^\infty$ is not directly needed for the main purpose of this investigation) were obtained by linear extrapolation of the respective apparent quantities to infinite dilution. The partial molar excess heat capacity $\bar{C}_{p,1}^{E,\infty}$ was then derived by subtracting the molar heat capacity of the pure solute. The experiments on cyclohexylamine solutions were carried out using 0.03 mol·kg^{-1} NaOH solutions instead of pure water to suppress the amine hydrolysis. It is assumed that this practice, adopted in the past by other investigators, yields results closely approximating the values for the neutral amine in pure water.

Table 2. Experimental Limiting Activity Coefficients γ_1^∞ (this work and literature) for Nitrobenzene, Aniline, and Cyclohexylamine in Water along with Their Estimated Uncertainties $s_{rel}(\gamma_1^\infty)^a$ and the Method of Measurement

T/K	γ_1^∞	$s_{rel}(\gamma_1^\infty)$	method^b	ref
		Nitrobenzene		
333.15	2447	0.05	RDIST	this work
333.15	2319	0.05	RDIST	this work
343.15	2149	0.05	RDIST	this work
353.15	1638	0.05	RDIST	this work
353.15	1659	0.05	RDIST	this work
372.85	1318	0.05	CIRC	this work
293.15	3597	0.05	SOL	11
303.15	3106	0.05	SOL	11
328.15	2532	0.05	SOL	11
288.15	3832	0.05	SOL	12
303.15	3328	0.05	SOL	12
279.15	4016	0.1	SOL	13
303.15	3311	0.05	SOL	13
323.15	2584	0.05	SOL	13
333.15	2188	0.05	SOL	13
298.15	3268	0.05	SOL	14
372.4	1002	0.2	CIRC	15
298.15	1433	0.5	IGS	16
283.15	3850	0.03	SOL	17
293.15	3520	0.03	SOL	17
303.15	3300	0.03	SOL	17
313.15	3100	0.03	SOL	17
		Aniline		
298.15	145	0.05	HSA	this work
333.15	130	0.03	RDIST	this work
343.15	121	0.03	RDIST	this work
343.15	119	0.03	RDIST	this work
353.15	111	0.03	RDIST	this work
372.47	92.7	0.03	CIRC	this work
313.15	138	0.05	CIRC	18
323.15	135	0.05	CIRC	19
356.28	135	0.2	EBUL	20
361.97	128	0.2	EBUL	20
366.84	119	0.2	EBUL	20
371.03	113	0.2	EBUL	20
298.15	134	0.5	IGS	16
		Cyclohexylamine		
298.15	19	0.05	HSA	this work
313.15	29.1	0.05	HSA	this work
333.15	36.7	0.1	RDIST	this work
343.15	44.8	0.1	RDIST	this work
353.15	51.2	0.1	RDIST	this work
372.65	64.5	0.1	CIRC	this work
372.82	53.5	0.1	CIRC	this work
372.82	64.6	0.1	CIRC	this work
298.15	17.4	0.2	IGS	16

[a] Relative combined standard uncertainty. [b] CIRC, circulation still method; EBUL, comparative ebulliometry; HSA, headspace analysis; IGS, inert gas stripping; RDIST, Rayleigh distillation method; SOL, solubility measurement.

Results and Discussion

The limiting activity coefficients determined in this work for nitrobenzene, aniline, and cyclohexylamine in water are listed, along with results gathered from the literature, in Table 2. The uncertainties given (relative combined standard uncertainties $s_{rel}(\gamma_1^\infty)$) take into account all possible sources of error. We estimated these uncertainties in a consistent manner so that within their limits the statistical coherence of all existing information on γ_1^∞, $\bar{H}_1^{E,\infty}$, and $\bar{C}_{p,1}^{E,\infty}$ for a given system was achieved. The γ_1^∞ data are displayed in van't Hoff coordinates in Figures 1 to 3. Mutual comparison of these values based on their thermodynamically consistent fit with related thermal data will be discussed below.

The saturated vapor pressures of pure solutes used in our calculations are given in Table 3. We selected these vapor pressure equations among other vapor pressure data and their representations available in the literature as the most reliable ones for the temperature range considered here. Nevertheless, except for aniline for which new accurate vapor pressure data

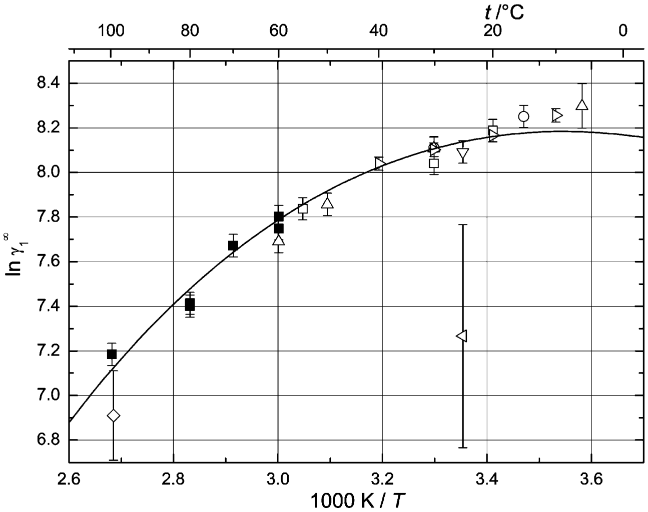

Figure 1. Limiting activity coefficient $\ln \gamma_1^\infty$ of nitrobenzene (1) in water (2) as a function of temperature. Experimental values are from Table 2: □, ref 11; ○, ref 12; △, ref 13; ▽, ref 14; ◇, ref 15; left-facing open triangle, ref 16; right-facing open triangle, ref 17; ■, this work. The solid line indicates the recommended temperature dependence obtained by simultaneous fit of γ_1^∞, $\bar{H}_1^{E,\infty}$, and $\bar{C}_{p,1}^{E,\infty}$ data by eq 9.

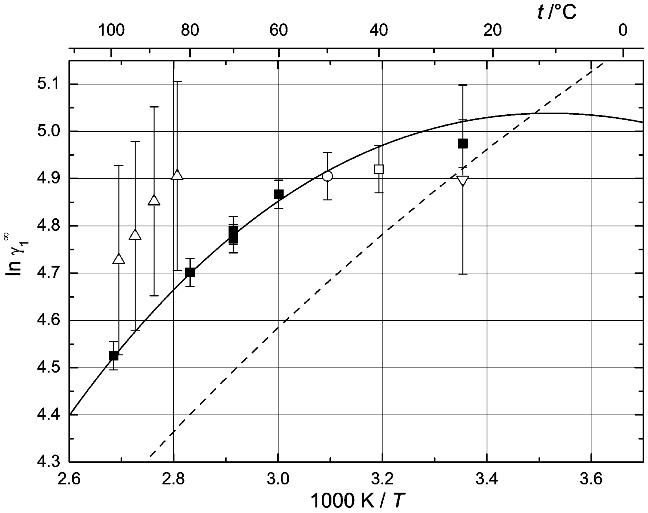

Figure 2. Limiting activity coefficient $\ln \gamma_1^\infty$ of aniline (1) in water (2) as a function of temperature. Experimental values are from Table 2: □, ref 18; ○, ref 19; △, ref 20; ▽, ref 16; ■, this work. The solid line indicates the recommended temperature dependence obtained by simultaneous fit of γ_1^∞, $\bar{H}_1^{E,\infty}$, and $\bar{C}_{p,1}^{E,\infty}$ data by eq 9. The dashed line is the prediction by the modified UNIFAC (Dortmund).

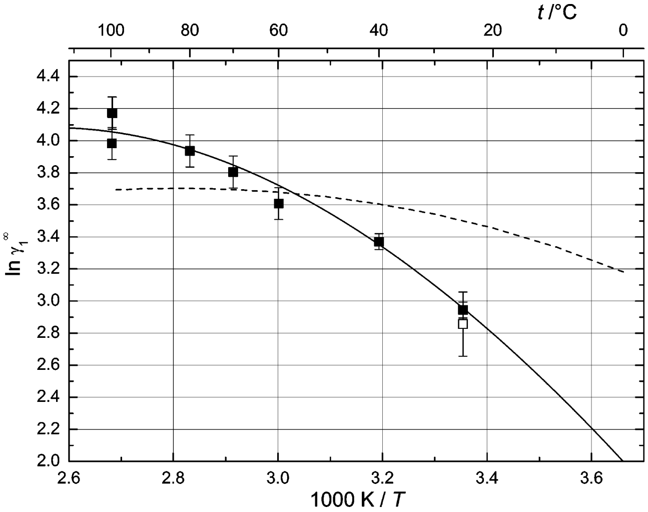

Figure 3. Limiting activity coefficient $\ln \gamma_1^\infty$ of cyclohexylamine (1) in water (2) as a function of temperature. Experimental values are from Table 2: □, ref 16; ■, this work. The solid line indicates the recommended temperature dependence obtained by simultaneous fit of γ_1^∞, $\bar{H}_1^{E,\infty}$, and $\bar{C}_{p,1}^{E,\infty}$ data by eq 9. Within the scale of the figure no difference between the three- and four-parameter fits is visible. The dashed line is the prediction by the modified UNIFAC (Dortmund).

at higher temperatures have been presented recently by Steele et al.,[22] the accuracy of the vapor pressure data is considerably compromise. The worst situation occurs at ambient temperatures and below where the solute vapor pressures attain lowest values (for nitrobenzene and aniline less than 100 Pa) and their uncertainties as high as 5 % to 10 % should be allowed for. Note that for aniline the extrapolation by the Wagner equation as given by Steele et al.[22] is preferred to existing direct vapor pressure measurements at lower temperatures. This extrapolation is consistent with room temperature calorimetric data on enthalpy of vaporization and pure liquid and ideal gas heat capacities. In addition, we found this extrapolation to be similar to that yielded by the Cox equation that is known for extrapolating well toward lower temperatures.[24] To avoid the propagation of large uncertainties in vapor pressures of solutes to $s_{\text{rel}}(\gamma_1^\infty)$ when determining γ_1^∞ at near ambient temperatures, we conveniently employed the HSA method, since this procedure does not require the knowledge of pure component vapor pressures. Note that also γ_1^∞ values inferred from liquid solubility measurements are free of vapor pressures errors.

Results of our heat capacity determinations are summarized in Table 4, together with their comparison with literature data. Involved in this table are also partial molar volumes at infinite dilution obtained as a byproduct of our $\bar{C}_{p,1}^{E,\infty}$ determinations. For nitrobenzene, because of its low aqueous solubility, the feasibility of our measurements was nearly borderline. Difficulties were encountered not only due to low differential signals between highly dilute solutions and the pure solvent water but also in the preparation of the solutions of accurately known concentration alone. As a consequence, measurement uncertainties for nitrobenzene are significantly larger than those for aniline or cyclohexylamine. No heat capacity data for aqueous nitrobenzene solutions have been found in the literature for comparison, the deviation of our $\bar{V}_1^\infty$ value from a recently reported more accurate literature one[25] being statistically acceptable. For aniline and cyclohexylamine there is an excellent agreement of the present $\bar{V}_1^\infty$ values and those from the literature. Heat capacity results for these two solutes can be compared only either to indirectly determined $\bar{C}_{p,1}^{E,\infty}$ literature values derived from the temperature dependence of $\bar{H}_1^{E,\infty}(T)$[8,27]

Table 3. Constants of Vapor Pressure Equations of Pure Solutes[a]

solute	equation	*A*	*B*	*C*	*D*	*E*	range/K	ref
nitrobenzene	Riedel−Planck[b]	85.828	−9493.8	−8.8595	6.8912E−18	6.0	279−719	21
aniline	Wagner[c]	−8.48712	3.35634	−4.10501	−4.00020		350−499	22
cyclohexylamine	Riedel−Planck[b]	149.080	−9336.7	−20.524	0.021378	1.0	255−615	21

[a] Vapor pressures of solvent water were obtained from equation given by Wagner and Pruss.[23] [b] $\ln(p^s/\text{kPa}) = A + B/(T/\text{K}) + C \ln(T/\text{K}) + D(T/\text{K})^E$. [c] $\ln(p^s/p_c) = (T_c/T)(AF + BF^{1.5} + CF^{2.5} + DF^5)$; $F = 1 - T/T_c$; $T_c = 705$ K; $p_c = 5630$ kPa.

Table 4. Experimental Partial Molar Volumes $\bar{V}_1^\infty$ (this work and literature), Partial Molar Heat Capacities $\bar{C}_{p,1}^\infty$, and Partial Molar Excess Heat Capacities $\bar{C}_{p,1}^{E,\infty}$ (this work and literature) at Infinite Dilution in Water at 298.15 K[a,b]

solute	$\bar{V}_1^\infty$ / $\mathrm{cm^3 \cdot mol^{-1}}$	$\bar{V}_1^\infty$(lit) / $\mathrm{cm^3 \cdot mol^{-1}}$	$\bar{C}_{p,1}^\infty$ / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\bar{C}_{p,1}^{E,\infty}$ / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\bar{C}_{p,1}^{E,\infty}$(lit) / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
nitrobenzene	96.4 ± 1.0	97.9 ± 0.2[25]	425 ± 8	244 ± 10	
aniline	89.43 ± 0.07	89.49 ± 0.02[26]	322 ± 3	131 ± 3	116,[27] 143[c,28]
cyclohexylamine	105.5 ± 0.2	105.4 ± 0.2[29]	470 ± 4	258 ± 5	269[8]

[a] The confidence intervals given correspond to combined standard uncertainties. [b] Heat capacities of pure liquid solutes used to calculate $\bar{C}_{p,1}^{E,\infty}$ values were from refs 30 and 31 (nitrobenzene, aniline) or ref 8 (cyclohexylamine). [c] At 303.55 K.

Table 5. Experimental Limiting Partial Molar Excess Enthalpies $\bar{H}_1^{E,\infty}$(lit) for Nitrobenzene, Aniline, and Cyclohexylamine in Water along with Their Estimated Uncertainties $s(\bar{H}_1^{E,\infty})$[a]

solute	T / K	$\bar{H}_1^{E,\infty}$ / $\mathrm{kJ \cdot mol^{-1}}$	$s(\bar{H}_1^{E,\infty})$ / $\mathrm{kJ \cdot mol^{-1}}$	ref
nitrobenzene	298.15	3.96	0.11	32
aniline	298.15	1.88	0.12	33
	298.15	1.38	0.3	34
	298.15	2.0	0.25	35
	293.15	1.22	0.04	27
	298.15	1.78	0.02	27
	305.15	2.63	0.03	27
	313.15	3.72	0.02	27
	298.15	1.83	0.02	36
cyclohexylamine	278.09	−27.91	0.03	8
	298.17	−22.52	0.04	8
	323.38	−15.86	0.01	8
	349.23	−9.35	0.04	8
	374.38	−3.45	0.1	8
	398.62	1.84	0.14	8
	298.15	−23.26	0.5	37

[a] Combined standard uncertainty.

or to a C_p measurement at different temperature.[28] While for cyclohexylamine, the literature value and our $\bar{C}_{p,1}^{E,\infty}$ value agree fairly well, for aniline a lack of agreement is seen. As one of the literature $\bar{C}_{p,1}^{E,\infty}$ values for aniline was inferred from a quadratic polynomial fit of only four $\bar{H}_1^{E,\infty}(T)$ points in a 20 K range[27] and the latter was obtained on an instrument designed mainly for high temperature/high-pressure measurements, more credit is placed here on the present $\bar{C}_{p,1}^{E,\infty}$ value.

Data on limiting partial molar excess enthalpies, which we collected from the literature, are listed in Table 5. For nitrobenzene, only one room temperature value has been found, but for the other two solutes $\bar{H}_1^{E,\infty}$ data are available at several temperatures, in case of cyclohexylamine covering even an extensive temperature range.

For each of the systems studied, the thermodynamic information gathered above was processed by a simultaneous correlation to establish reliable temperature dependence of γ_1^∞. The following equation was used for representing the temperature dependence of γ_1^∞:

$$\ln \gamma_1^\infty = A + B/\tau + C \ln \tau + D\tau \tag{9}$$

where A, B, C, and D are adjustable parameters and $\tau = T/(298.15\mathrm{K})$. All measured and literature data were treated together using the weighted least-squares method to evaluate the parameters of eq 9. In the objective function

$$S = \sum_{i=1}^{n_G} [\ln \gamma_{1,i}^\infty(\mathrm{exp}) - \ln \gamma_{1,i}^\infty(\mathrm{calc})]^2/s^2(\ln \gamma_{1,i}^\infty) + \sum_{i=1}^{n_H} [\bar{H}_{1,i}^{E,\infty}(\mathrm{exp}) - \bar{H}_{1,i}^{E,\infty}(\mathrm{calc})]^2/s^2(\bar{H}_{1,i}^{E,\infty}) + \sum_{i=1}^{n_C} [\bar{C}_{p,1,i}^{E,\infty}(\mathrm{exp}) - \bar{C}_{p,1,i}^{E,\infty}(\mathrm{calc})]^2/s^2(\bar{C}_{p,1,i}^{E,\infty}) \tag{10}$$

the data were weighted according to their uncertainties (standard deviations), which we assigned on the basis of our critical evaluation. All possible sources of error were considered, and the contributions were combined according to the error propagation law. For literature data, the first estimates of the uncertainties were based on information given in the original source from which the data were extracted. When necessary, the uncertainties were re-adjusted by trail and error to obtain the coherence of all data in the statistical sense. The goodness-of-fit test for the standard deviation of fit was used to indicate the coherence. Statistically reasonable sizes of individual residuals and their distribution among the three properties were considered as additional constraints.

For each of the systems studied, the calculated parameters of eq 9 are given together with the standard deviation of fit, the number of underlying experimental data points, and the temperature where γ_1^∞ attains its maximum in Table 6. The recommended temperature dependences of γ_1^∞ established by the fits are plotted in the van't Hoff coordinates in Figures 1 to 3. The probable data uncertainties are those listed in Tables 2, 4, and 5.

For nitrobenzene and aniline, the existing data justified the use of eq 9 in its three-parameter form only. For cyclohexylamine, accurate literature data on $\bar{H}_1^{E,\infty}(T)$ in a broad temperature range enabled us to apply the four-parameter form of eq 9. The comparison of fitting performances of the four- and three-parameter forms showed the superiority of the former one giving a fully adequate representation of experimental data. Nevertheless, as concerns solely $\gamma_1^\infty(T)$ in the range from 273 K to 373 K, the difference between the four- and three-parameter fits is within 1 % in γ_1^∞ and hence entirely negligible.

As seen from Figure 1, for nitrobenzene there is a good mutual agreement of γ_1^∞ values obtained from literature solubility data available at $T \leq 333$ K and γ_1^∞ values obtained by the present VLE measurements by RDIST and CIRC methods at $T \geq 333$ K. All these data follow closely the fitting line, their temperature trend being thus in accord with calorimetric information on the dissolution enthalpy and heat capacity. The γ_1^∞ value inferred from the inert gas stripping measurement of Altschuh et al.[16] is an apparent outlier; therefore, it was labeled with an appropriately enhanced uncertainty. To a lesser degree, the circulation still measurement by Hwang et al.[15] appears to be in error.

For aniline (Figure 2) one can see also a very good mutual agreement between the present measurements carried out by the various techniques (CIRC, RDIST, and HSA) as well as their reasonable accord with a few existing literature data, the ebulliometric measurements of Moore et al.,[20] which deviate systematically from all other data, being an exception. Note that the ebulliometric method is well-suited for systems having relative volatility close to unity, so for aniline in water, exhibiting in the temperature range in question $\alpha_{12}^\infty \geq 5$, the measurement is expected to be less accurate. The simultaneous fit of all available γ_1^∞, $\bar{H}_1^{E,\infty}$, and $\bar{C}_{p,1}^{E,\infty}$ data approximating well

Table 6. Parameters of Equation 9[a] Obtained by Simultaneous Fit of γ_1^∞, $\bar{H}_1^{E,\infty}$, and $\bar{C}_{p,1}^{E,\infty}$ Data, Number of Respective Underlying Data Points (n_G, n_H, n_C), Standard Deviation of Fit s, and Temperature T_{max} Where γ_1^∞ Is Maximum

solute	A	B	C	D	$n_G/n_H/n_C$	s[b]	T_{max}/K
nitrobenzene	36.4094	−28.2719	−29.9023		22/1/1	1.19	282
aniline	19.6708	−14.6501	−15.3761		13/8/ 2	1.15	284
cyclohexylamine[c]	44.2138	−49.8025	−49.2859	8.54470	9/ 7/ 1	1.19	390
	43.2345	−40.2771	−31.2148			4.91	385

[a] Recommended temperature dependence for limiting activity coefficient (273 to 373) K. [b] $s = [S_{min}/(n - p)]^{1/2}$; S is given by eq 10, p is the number of adjustable parameters. [c] Four-parameter form of eq 9 gives the fully adequate fit.

the temperature course of our VLE measurements proves their full consistency with the respective thermal data.

For cyclohexylamine, the consistency within experimental errors of our equilibrium measurements with calorimetric information is demonstrated in Figure 3. Here, the only literature γ_1^∞ value inferred from the measurements of Altschuh et al.[16] is seen to be in good agreement with the present results.

Like for many other more-or-less hydrophobic solutes in water, also for all the three solutes studied here, $\gamma_1^\infty(T)$ is non-monotonic exhibiting a maximum. For essentially hydrophobic solutes, this γ_1^∞ maximum, corresponding to their aqueous solubility minimum, occurs typically at slightly subambient temperatures, indicating that the dissolution process is mainly entropy controlled at near-ambient conditions. Nitrobenzene and aniline belong to this class of solutes. The behavior of cyclohexylamine follows, however, a distinctly different pattern. Despite of a closely similar chemical structure with aniline, cyclohexylamine is much less hydrophobic, apparently because of its more efficient hydrogen bonding with the solvent water. At ambient T the dissolution of cyclohexylamine in water is then highly exothermic, which heavily promotes its aqueous solubility, and it is only at a higher T above the normal boiling point of water where these hydrogen bonds are to a great extent broken and the maximum in γ_1^∞ occurs.

The leading group contribution method, modified UNIFAC (Dortmund),[38] with the most recent parameter matrix (2005)[39] was tested in the prediction of these $\gamma_1^\infty(T)$ dependences. The results of the prediction are shown for aniline and cyclohexylamine in Figures 2 and 3, respectively; for nitrobenzene the calculation cannot be done because the necessary interaction parameters are not available. The predictions can be considered quite reasonable but yet far from perfect. It is believed that the recommended $\gamma_1^\infty(T)$ presented in this work can be helpful for further improvement and/or extension of modified UNIFAC predictions.

Furthermore, in addition to the recommended temperature dependences of the limiting activity coefficients, analogous recommendations were derived for the temperature dependences of the Henry's law constants $k_H(T)$, combining the $\gamma_1^\infty(T)$ results from Table 6 with $p_1^s(T)$ from Table 3 ($k_H = \gamma_1^\infty p_1^s$). To obtain an analytical expression for the temperature dependence of the Henry's law constant, k_H values were generated at 21 equidistant temperatures (5 K increment) covering the temperature range from 273.15 K to 373.15 K and fitted with the following equation:

$$\ln(k_H/\text{kPa}) = A + B/\tau + C \ln \tau \qquad (11)$$

Table 7. Parameters of Equation 11[a]

solute	A	B	C
nitrobenzene	64.5260	−59.7840	−38.4032
aniline	48.9325	−46.4403	−24.6450
cyclohexylamine	66.7211	−63.4764	−37.2838

[a] Recommended temperature dependence for Henry's law constant (273 to 373) K.

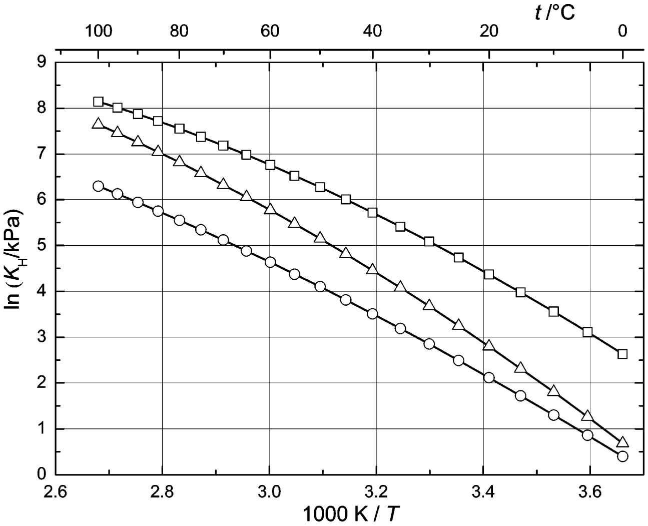

Figure 4. Henry's law constants k_H of −□−, nitrobenzene; −○−, aniline; and −△−, cyclohexylamine in water as a function of temperature.

Table 8. Recommended Values of Limiting Activity Coefficients γ_1^∞ and Henry's Law Constants k_H along with Their Relative Standard Uncertainties

T/K	γ_1^∞	$s_{rel}(\gamma_1^\infty)$	k_H/kPa	$s_{rel}(k_H)$
		Nitrobenzene		
273.15	3530	0.02	13.9	0.10
298.15	3420	0.02	115	0.05
323.15	2745	0.02	531	0.05
373.15	1225	0.03	3430	0.04
		Aniline		
273.15	152	0.03	1.48	0.10
298.15	152	0.02	12.1	0.05
323.15	136	0.02	60.4	0.04
373.15	91.4	0.02	543	0.02
		Cyclohexylamine		
273.15	7.37	0.04	1.99	0.10
298.15	19.2	0.03	25.8	0.05
323.15	35.1	0.03	173	0.05
373.15	57.8	0.03	2085	0.04

The calculated parameters of eq 11 are given in Table 7, and the respective temperature dependences of k_H are plotted in the van't Hoff coordinates in Figure 4. Nitrobenzene, despite having the lowest vapor pressure of the solutes studied, exhibits the highest volatility from the dilute aqueous solutions thanks to its enormous γ_1^∞ values. On the other hand, for aniline, whose dilute aqueous solutions are substantially less nonideal, the Henry's law constants attain the lowest values, being nearly order of magnitude less than those for nitrobenzene. The $k_H(T)$ courses for nitrobenzene and aniline in Figure 4 are seen to be almost parallel; $k_H(T)$ for cyclohexylamine, located between the two, however breaks this pattern, being considerably steeper. Note that the respective difference in the hydration enthalpies comes from the distinctly different enthalpies of dissolution (cf.

Table 5) overwhelming the difference in enthalpies of vaporization of the pure solutes.[40] The maxima in the Henry's law constant that are for this type of solutes observed at superambient conditions occur at temperatures clearly superior to the range of the treated experimental data and cannot be estimated even on semiquantitative level.

Recommended values of γ_1^∞ and k_H, along with their relative combined standard uncertainties calculated by the error propagation law, are given at several representative temperatures in Table 8. These uncertainties are typically within 3 % and 5 % for γ_1^∞ and k_H, respectively, except for k_H at subambient temperatures where one should expect the standard uncertainty as high as 10 % due to the uncertainty of pure solute vapor pressure data.

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Appendix A

The mass balance for an infinitesimal extent of an equilibrium one-stage distillation of a binary solution leads to the following differential equation:[3]

$$\mathrm{d}n/n = \mathrm{d}x_1/(y_1 - x_1) \tag{A1}$$

which relates the compositions of the equilibrium phases to the molar amount of the solution remaining in the distillation flask. Let us consider a basic solute (e.g., amine) that undergoes partial hydrolysis in its dilute aqueous solution according eq 4. Since in the liquid phase the solute is contained in both the neutral (B) and the protonized form (BH^+), then

$$x_1 = x_B + x_{BH^+} \tag{A2}$$

while in the vapor phase only neutral species are present and hence

$$y_1 = y_B \tag{A3}$$

The liquid-phase mole fractions of the neutral x_B and the protonized species x_{BH^+} can be further related to the total liquid mole fraction of the solute through the degree of solute hydrolysis ξ:

$$x_B = (1 - \xi)x_1 \tag{A4}$$

$$x_{BH^+} = \xi x_1 \tag{A5}$$

where ξ is given by the equilibrium condition for the hydrolysis (eq 5). At high dilutions the condition of vapor−liquid equilibrium requires the vapor-phase mole fraction of the volatile solute species y_B to be proportional to its liquid-phase mole fraction:

$$y_B = \alpha_{12}^\infty x_B \tag{A6}$$

where α_{12}^∞ is the solute limiting relative volatility. Then, using gradually eq A2, A3, A6, A4, and A5 for substitution into eq A1, one gets

$$\frac{\mathrm{d}n}{n} = \frac{\mathrm{d}x_1}{x_1[\alpha_{12}^\infty(1 - \xi) - 1]} \tag{A7}$$

Finally, $\mathrm{d}n/n$ and $\mathrm{d}x_1/x_1$ in eq A7 can be well-approximated at high dilution by $\mathrm{d}m/m$ and $\mathrm{d}b_1/b_1$, respectively, where m is the mass of the solution and b_1 is the total solute molality, yielding

$$\frac{\mathrm{d}m}{m} = \frac{\mathrm{d}b_1}{b_1[\alpha_{12}^\infty(1 - \xi) - 1]} \tag{A8}$$

Equation A8 is the differential equation controlling the Rayleigh distillation of highly dilute aqueous solutions of solutes that undergo partial hydrolysis. For a finite extent of distillation, eq A8 becomes

$$\ln\frac{m}{m^0} = \int_{b_1^0}^{b_1} \frac{\mathrm{d}b_1}{b_1[\alpha_{12}^\infty(1 - \xi) - 1]} \tag{A9}$$

the right-hand side requiring numerical integration. Iterative calculations are further needed to obtain α_{12}^∞ (or γ_1^∞) from experimental Rayleigh distillation data, that is, from the measured solution masses (m^0 and m) and the respective molalities ($b_1{}^0$ and b_1).

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