J. Chem. Eng. Data **2001,** *46,* 1533−1539

Measurement of Aqueous Solubility of Hydrophobic Volatile Organic Compounds by Solute Vapor Absorption Technique: Toluene, Ethylbenzene, Propylbenzene, and Butylbenzene at Temperatures from 273 K to 328 K

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An apparatus and procedure are described for measuring the aqueous solubility of hydrophobic volatile compounds. The method employs the solute vapor absorption technique (SVA) for preparation of the saturated solution followed by subsequent off-line HPLC analysis of the cosolvent adjusted aqueous solution. The method circumvents several drawbacks encountered with the traditional liquid−liquid batch contacting ("shake-flask") system and yields reproducible and precise results (3%). Correct performance of the method was demonstrated using benzene as a test solute. Using the method, aqueous solubilities of lower alkylbenzenes (toluene, ethylbenzene, propylbenzene, and butylbenzene) were determined in the temperature range from 273 K to 328 K. The results are compared with available literature information. An excellent agreement found for toluene gradually deteriorates for higher homologues, with the largest discrepancy occurring at the lowest temperatures. The lack of reliable information for a decisive conclusion at subambient temperatures appears to be rather general, calling for continued experimental effort.

Introduction

Knowledge of the aqueous solubility of organic compounds is required for practical applications and theoretical studies in a number of disciplines such as physical and environmental chemistry, chemical engineering, and the biological, pharmaceutical, and medical sciences. For sparingly soluble hydrophobic liquids (mole fraction solubility $x_1^{sol} < 10^{-3}$), the aqueous solubility represents a unique experimental thermodynamic parameter that is closely related to their limiting activity coefficient in water ($\gamma_1^{\infty} = 1/x_1^{sol}$), a fundamental thermodynamic quantity characterizing aqueous solution nonideality and governing fluid phase equilibria in the highly dilute aqueous solutions.

Although a seemingly simple task, the determination of low aqueous solubilities of hydrophobic substances is complicated by severe difficulties that adversely affect the accuracy of results and their intermethod and interlaboratory agreement. Major sources of error in the routinely applied batch liquid contacting technique ("shake-flask" method) are as follows: (i) mechanical agitation of two-phase liquid system causes dispersion rather than true dissolution of the hydrophobic substance in water and hence supersaturation; (ii) in nonagitated systems, the equilibration process is very slow, and any premature termination of the phase contacting results in incomplete saturation; (iii) due to low concentrations, solute losses by adsorption, volatilization, and sample manipulation become crucial.

With the aim to suppress the drawbacks of the conventional batch liquid contacting method, various other techniques for the determination of the aqueous solubility of hydrophobic compounds have been proposed that modify the processes of equilibration and sample manipulation. In the generator column technique of May et al.,[1] which has proved useful mainly for nonvolatile substances of very low solubility such as polyaromatic hydrocarbons, the saturated solution is generated by pumping water through a column packed with an inert support coated with the compound of interest. For volatile hydrophobic solutes, the saturated solution may also be prepared by absorbing the solute in water from the vapor phase[2] or, alternatively, instead of measuring liquid−liquid equilibrium, air−water partitioning can be determined by a suitable technique such as inert gas stripping (IGS),[3−5] equilibrium partitioning in a closed system (EPICS),[6,7] and an exponential saturator (EXPSAT).[8] As a matter of fact, the EXPSAT method, which has been developed recently in this laboratory, and the procedure of Sanemasa et al.[2] both deal with the solute vapor absorption process. However, whereas the former method consists of measuring the rate of solvent water saturation by the solute vapor, the latter employs the solute vapor absorption merely to prepare the saturated solution.

In this paper we describe our new implementation of a solute vapor absorption (SVA) method inspired by the ideas of Sanemasa et al. and those of the exponential saturator and apply it for the determination of the aqueous solubility of lower *n*-alkylbenzenes (toluene, ethylbenzene, propylbenzene, and butylbenzene) over a broad temperature range. The interest in the aqueous solubility of alkylbenzenes stems again from both practical and theoretical aspects. As important petrochemicals produced on a large scale, alkylbenzenes are contained in automotive and aviation gasoline and other fuel formulations and are widely used in chemical industry as solvents and intermediates; their widespread use thus presents a hazard for the

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10.1021/je010172r CCC: $20.00

environment and human health.[9,10] In thermodynamics and biothermodynamics, alkylbenzenes perform a role of model probes in the investigation of hydrophobic hydration and protein denaturation.[11−13]

The aqueous solubility and air−water partitioning of alkylbenzenes have been measured by many researchers,[14] yet, reliable data of good accuracy are not as ample as could be expected. Most data have been measured only at the single temperature of 298 K. Although the temperature dependence of solubility for alkylbenzenes in water exhibiting a non-monotonic behavior (minima occur around the ambient temperature) is of great interest, relevant measurements are rather scarce and, with the exception of the most recent work of Sawamura et al.,[15] do not typically extend over more than 30 K and to temperatures below ambient. In general, the amount and quality of available data are not uniform for individual homologues of alkylbenzene series but considerably decrease with the prolongation of the alkyl substituent of the homologue. Whereas for benzene and nearly so for toluene, the available information can be considered adequate so that reliable recommended temperature dependences of γ_1^∞ in water over the temperature interval from 273 K to 373 K could be recently presented,[16] for ethylbenzene, propylbenzene, and butylbenzene the situation is less satisfactory and additional experimental effort is required for such recommendations.

Experimental Section

Materials. Benzene (p.a.) and toluene (p.a.) supplied by Lachema (Neratovice, Czech Republic) were fractionally distilled, and final products were dried and stored with 0.4 nm molecular sieves. Ethylbenzene (99%), propylbenzene (98%), and butylbenzene (99+%) were received from Aldrich Chemical Co. and used directly from freshly opened bottles. For each of these aromatic hydrocarbons, a purity of >99% was confirmed by liquid chromatography and gas chromatography. 2-Propanol (AR grade, 99.7%) obtained from Lachema was employed as auxiliary solvent and the HPLC mobile phase without further purification. Water was distilled and subsequently treated by a Milli-Q water purification system (Millipore, Milford, MA).

Method, Apparatus, and Procedure. The method developed in this work employs the solute vapor absorption technique (SVA) for preparation of the saturated solution followed by subsequent off-line HPLC analysis of the cosolvent adjusted aqueous solution. In the SVA, an inert gas presaturated first by the vapor of the solute + water heterogeneous mixture is passed through the water solvent in which the solute is continuously absorbed until the liquid phase is saturated. The apparatus used for solubility measurements is shown schematically in Figure 1. It consists of two parts: a gas saturator (A) and a liquid saturator (B). The purpose of the gas saturator is to generate a stream of the equilibrium gas phase corresponding to the heterogeneous hydrocarbon + water mixture. The purpose of the liquid saturator is to generate the saturated aqueous solution of the hydrocarbon by absorbing the hydrocarbon from the gas phase generated in the former part into the solvent water. Both parts of the apparatus are all-glass jacketed devices that, during the saturation experiment, are connected through a ground glass joint and thermostated by a water circulating bath (RC 6 CP, Lauda, Germany) to the same temperature. The temperature of the water bath was measured with calibrated standard mercury thermometers (Karl Schneider, Wertheim, Germany) to ±0.01 K. The gas saturator was provided with an inlet tube (1) that served as a port to load the liquids and as an inlet for the inert carrier gas. The respective saturation chamber (2) had a volume of ∼15 cm^3 and was divided into three stages by fritted glass. Through a connecting tube (3) the stream of the generated equilibrium vapor was conducted into the liquid saturator, where the solvent water was dispersed through a fritted glass tip (4) into small-diameter bubbles. The volume of the liquid saturator was ∼150 cm^3, and its contents were mixed with a magnetic stirrer (5). The solute from the gas phase was partially absorbed by the solvent water in the liquid saturator; its concentration in the liquid phase thus gradually increased to the solubility limit. The gas phase flow left part B of the apparatus via the outlet tube (6). For experiments at a higher temperature than ambient, this tube was heated by an electric heating tape to prevent condensation.

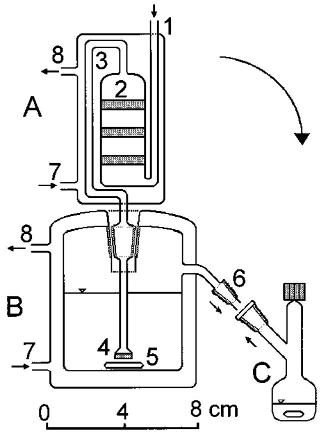

Figure 1. Solubility apparatus for the SVA method: A, gas saturator; B, liquid saturator; C, sampling vessel; 1, inlet tube; 2, gas saturation chamber; 3, connecting tube; 4, fritted glass tip; 5, magnetic stirrer; 6, outlet tube; 7, input of thermostating water; 8, output of thermostating water.

The experimental procedure started with loading ∼100 cm^3 of the solvent water into the liquid saturator and ∼5 cm^3 of the hydrocarbon + water mixture into the gas saturator. The temperature was set and the flow of the inert gas (N_2) established. The flow rate of N_2 was maintained at ∼6 cm^3/min by an electronic flow rate controller (Laboratorní Přístroje, Praha, Czech Republic); such low flow rates of the inert gas have been previously found to lead to the complete equilibration in the stripping and absorption flow processes under similar conditions.[5,8] Provided an estimate of x_1^{sol} is available, the time to achieve effectively the saturation of the solvent water in the liquid saturator can be calculated. Following the theory of exponential saturator,[8] the time needed for 99.9% approach to the saturation is

$$t_{0.999} = \frac{x_1^{\text{sol}} n_2 RT(P - P_1^{\text{s}} - P_2^{\text{s}})}{DP(P - P_2^{\text{s}})}\left(0.999 - \frac{P - P_1^{\text{s}} - P_2^{\text{s}}}{P_1^{\text{s}}}\ln 0.001\right) \tag{1}$$

where P_1^{s} and P_2^{s} are the vapor pressures of the solute and the solvent, respectively, n_2 is the molar amount of the solvent water in the liquid saturator, and D is the neat carrier gas flow rate at experimental temperature T and pressure P. Equation 1 corresponds to eq 9 of ref 8; their only difference comes from the fact that in the present case the vapor saturator is filled with a heterogeneous mixture of a hydrophobic solute and water, whereas in ref 8 the vapor saturator contained just the pure solute. The saturation experiments in this work were performed over an extended period of time exceeding $t_{0.999}$ by at least 25%. Repeated experiments with still longer times of saturation lead to the same results, thus proving the attainment of complete saturation. As no attendance of experimenter is needed, the saturation was typically carried out overnight.

When the saturation was completed, the carrier gas flow was stopped and the exhaust manifold at the outlet (6) was replaced by a matching test tube. By tilting the stand with the apparatus a portion of the saturated solution was transferred into the test tube. This first portion was used to wash the outlet tube and was discarded. The sample for analysis was taken subsequently using a special sampling vessel (C) shown in Figure 1. This vessel containing a previously weighed amount of the auxiliary solvent (2-propanol) and a magnetic stirrer was attached to the apparatus by means of the ground glass joint. The amount of the saturated solution taken was determined by differential weighing, and the contents of the sampling vessel were well mixed. Routinely, two samples were taken to check the sampling process.

The samples were analyzed using a high-performance liquid chromatograph (Ecom, Prague, Czech Republic) equipped with a model LCP 4100 HPLC pump, a model LCD 2082 UV detector, and a C18 glass analytical column. The HPLC pump was operated in the constant flow rate mode, pumping a mixture 4:1 (v/v) of 2-propanol with water used as the mobile phase at 0.50 cm^3/min. Signal acquisition and integration were achieved by an interfaced personal computer using CSW chromatographic data station software (DataApex, Prague, Czech Republic). For each solute, the wavelength of the UV detection was set to the value corresponding to its local absorbance maximum determined in a preliminary experiment. The detector was calibrated by four standard solutions containing known amounts of solute dissolved in the auxiliary solvent 2-propanol. Note that using 2-propanol as the auxiliary solvent is essential in both the sampling and analysis processes: 2-propanol decreases appreciably the volatility of alkylbenzenes from their aqueous solutions, adjusts the character of the sample to the HPLC mobile phase and its concentration to the range of detector, and serves as the solvent for preparation of calibration samples. Due to the low level of the respective concentrations, the standard solutions were prepared in two steps, diluting a suitable stock solution prepared first. The calibration confirmed the validity of the Lambert−Beer law in the given range of concentrations. The analysis of each sample was replicated 6−10 times.

Results and Discussion

The SVA method was verified with benzene as a test solute. The aqueous solubility or limiting activity coefficient in water for benzene at 298.15 K is known with very good accuracy. The IUPAC recommended value[17] of solubility is $x_1^{\mathrm{sol}} = (4.09 \pm 0.05) \times 10^{-4}$, and γ_1^{∞} from the most recent recommendation[16] of its temperature dependence is $\gamma_1^{\infty} = 2470 \pm 5$, the uncertainties given being the estimated standard deviations. Our 10 repeated measurements carried out by the SVA method at 298 K resulted in $x_1^{\mathrm{sol}} = (4.08 \pm 0.07) \times 10^{-4}$ or $\gamma_1^{\infty} = 2451 \pm 40$, which is in an excellent agreement with both of the above-mentioned recommendations.

The aqueous solubility of toluene, ethylbenzene, propylbenzene, and butylbenzene was determined at seven temperatures in the range from 273 K to 328 K. The experimental results are summarized in Table 1; they are given in the form of molar concentrations *S*, mole fractions x_1^{sol}, and limiting activity coefficients γ_1^{∞}. Considering the propagation of errors in experimental variables and the observed reproducibility of repeated measurements, the uncertainty of the values reported in Table 1 is estimated to be within 3% except for butylbenzene, for which the uncertainty of ∼5% is to be expected due to a relatively worse reproducibility of the analytical determinations.

Table 1. Experimental Solubilities *S*, Mole Fraction Solubilities x_1^{sol}, and Limiting Activity Coefficients[a] γ_1^{∞} for Alkylbenzenes in Water as a Function of Temperature *T*

T/K	$S/(10^{-3}\cdot\mathrm{mol\cdot dm^{-3}})$	$x_1^{\mathrm{sol}}\cdot 10^6$	γ_1^{∞}
	Toluene		
273.65	6.11	110	9060
278.15	5.99	108	9260
288.15	5.88	106	9430
298.15	6.03	109	9200
308.15	6.40	116	8610
318.15	6.86	125	7970
328.15	7.64	140	7140
	Ethylbenzene		
273.65	1.59	28.6	35000
278.15	1.57	28.3	35300
288.15	1.56	28.2	35500
298.15	1.60	28.9	34600
308.15	1.67	30.2	33100
318.15	1.77	32.3	31000
328.15	2.01	36.9	27100
	Propylbenzene		
273.65	0.387	6.98	143000
278.15	0.381	6.86	146000
288.15	0.373	6.73	149000
298.15	0.401	7.24	138000
308.15	0.434	7.86	127000
318.15	0.519	9.46	106000
328.15	0.619	11.34	88200
	Butylbenzene		
273.65	0.0860	1.55	645000
278.15	0.0855	1.54	648000
288.15	0.0843	1.52	656000
298.15	0.0913	1.65	605000
308.15	0.108	1.95	513000
318.15	0.131	2.39	418000
328.15	0.156	2.86	349000

[a] $\gamma_1^{\infty} = 1/x_1^{\mathrm{sol}}$.

The observed temperature dependence of x_1^{sol} (γ_1^{∞}) exhibits for all of the alkylbenzenes the same general pattern with a characteristic, rather shallow minimum (flat maximum) at a temperature slightly below room temperature. For each of the four alkylbenzenes, we fitted the temperature dependence to the following equation originating from the assumption of temperature-independent heat capacity of solution

$$\ln \gamma_1^{\infty} = A + B/\tau + C \ln \tau \tag{2}$$

where $\tau \equiv T/T_0$ and the scaling temperature $T_0 = 298.15$ K. Although it is known that $\Delta_{\mathrm{sol}}C_{p,1}^{\infty}$ decreases with temperature,[18] the extent and accuracy of γ_1^{∞} data do not justify more complex fits with a greater number of adjustable parameters. Values of adjustable parameters *A*, *B*, and *C* and respective standard deviations of fit are reported in Table 2. The fittings clearly demonstrate the smoothness of the measured data, reflecting, as expected, a somewhat enhanced scatter for butylbenzene.

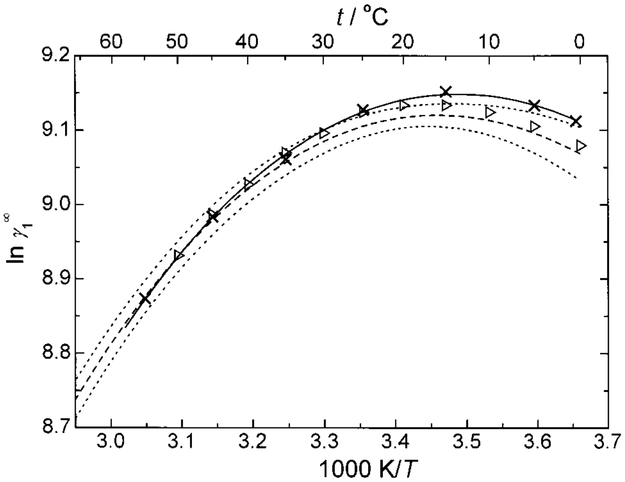

Figure 2. Limiting activity coefficient γ_1^∞ of toluene (1) in water (2) as a function of temperature: ×, this work, SVA; —, fit as given in Table 2 of experimental data from this work; - - -, recommended fit with its 95% confidence band (dotted line), Hovorka et al.;[16] right-pointing triangle, Sawamura et al.[15]

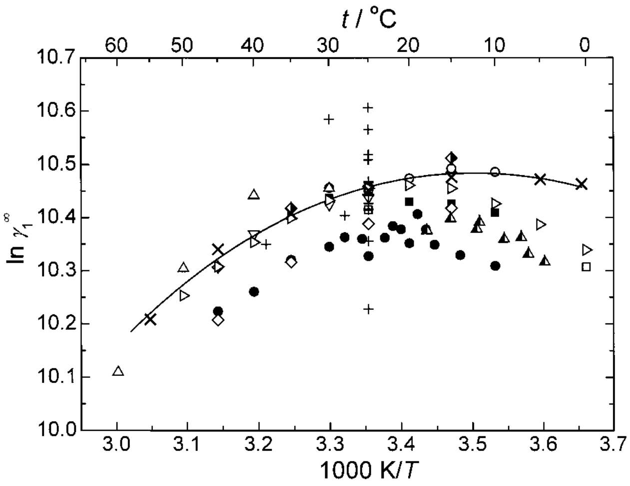

Figure 3. Limiting activity coefficient γ_1^∞ of ethylbenzene (1) in water (2) as a function of temperature: × this work, SVA; —, fit as given in Table 2 of experimental data from this work; □, Polak and Lu;[19] ◭, Brown and Wasik;[20] ◇, Sanemasa et al.;[21] half-solid diamond, Sanemasa et al.;[2] ●, Owens et al.;[22] ○, Ashworth et al.;[7] ■, Perlinger et al.;[23] ▽, Robbins et al.;[24] △, Chen and Wagner;[25] right-pointing triangle, Sawamura et al.;[15] +, single points at 298.15 K from refs 3 and 26−38, at 301.15 K from ref 39, at 303.15 K from ref 40, and at 311.5 K from ref 41.

Table 2. Parameters of Equation 2 Used To Fit the Experimental Results from Table 1 along with the Standard Deviation of Fit

compound	*A*	*B*	*C*	*s*
toluene	39.6555	−30.5310	−31.7487	0.004
ethylbenzene	37.9088	−27.4511	−28.6566	0.012
propylbenzene	62.2855	−50.4389	−52.9316	0.013
butylbenzene	66.2417	−52.9459	−56.2510	0.023

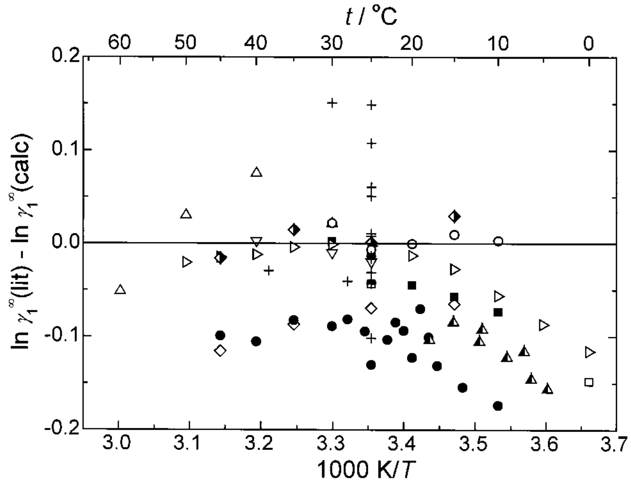

Figure 4. Limiting activity coefficient γ_1^∞ of ethylbenzene (1) in water (2) as a function of temperature. Deviation plot relative to the fit of present SVA measurements: □, Polak and Lu;[19] ◭, Brown and Wasik;[20] ◇, Sanemasa et al.;[21] half-solid diamond, Sanemasa et al.;[2] ●, Owens et al.;[22] ○, Ashworth et al.;[7] ■, Perlinger et al.;[23] ▽, Robbins et al.;[24] △, Chen and Wagner;[25] right-pointing triangle, Sawamura et al.;[15] +, single points at 298.15 K from refs 3 and 26−38, at 301.15 K from ref 39, at 303.15 K from ref 40, and at 311.5 K from ref 41.

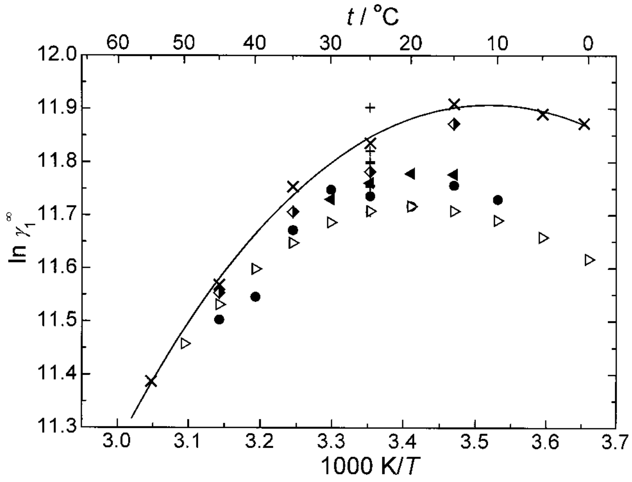

Figure 5. Limiting activity coefficient γ_1^∞ of propylbenzene (1) in water (2) as a function of temperature: ×, this work, SVA; —, fit as given in Table 2 of experimental data from this work; left-pointing triangle, DeVoe et al.;[42] half-solid diamond, Sanemasa et al.;[2] ●, Owens et al.;[22] right-pointing triangle, Sawamura et al.;[15] +, single points at 298.15 K from refs 4, 26, 31−34, and 36.

The results of our measurements by the SVA method have been duly compared with data available in the literature. The limiting activity coefficient was used as a suitable quantity for this comparison, which enables us to employ apart from data on liquid−liquid solubilities also data on gas−liquid partitioning. The comparison can be seen in Figures 2−6. Only superior data are plotted in these figures, evident outliers being excluded intentionally. The temperature dependence of the limiting activity coefficient of toluene in water has been recently examined by us in detail. The resulting recommended fit with its confidence limits is used in Figure 2 to represent a rather extensive literature information for this solute. The only literature data plotted explicitly in Figure 2 are those of Sawamura at al.[15] because these new measurements appeared after our recommendation had been published. It can be seen from Figure 2 that the present solubility measurements made with the SVA method, the new measurements by Sawamura et al., and the recent recommended temperature dependence are all in excellent agreement, the maximum deviation not exceeding 5% in γ_1^∞.

Figure 3 compares numerous data available for ethylbenzene in water. For the sake of lucidity, the data are also shown in Figure 4 in the form of a deviation plot relative to the fit of present SVA measurements. Our results exhibit excellent agreement with gas−liquid partitioning (EPICS) measurements of Ashworth et al.,[7] SVA

Table 3. Temperatures of Maximum γ_1^∞, Enthalpies, and Heat Capacities of Solution at Infinite Dilution for Alkylbenzenes in Water[a]

	T_{max}/K		$\Delta_{sol}H_1^\infty$(298 K)/(kJ·mol^{-1})		$\Delta_{sol}C_{p,1}^\infty$/(J·K^{-1} ·mol^{-1})	
compound	this work	lit.	this work	lit.	this work	lit.
toluene	287 ± 1	289 ± 2[16,b] 291.6 ± 0.2[44,c] 297[25,e] 289 ± 1[15,e]	3.0 ± 0.1	2.39 ± 0.35[16,b] 1.73 ± 0.04[44,c] 0.37[25,e] 2.5 ± 0.04[15,e]	260 ± 10	264 ± 17[16,b] 263 ± 13[44,c] 351[25,e] 287 ± 6[15,e] 305[18,d]
ethylbenzene	286 ± 2	291.8 ± 0.2[44,c] 295 ± 2[22,e] 285[25,e] 293 ± 1[15,e]	3.0 ± 0.2	2.02 ± 0.04[44,c] 1.3 ± 0.6[22,e] 4.38[25,e] 1.85 ± 0.07[15,e]	240 ± 20	318 ± 13[44,c] 470 ± 100[22,e] 338[25,e] 385 ± 10[15,e]
propylbenzene	284 ± 1	292.3 ± 0.3[44,c] 292 ± 3[22,e] 292 ± 1[15,e]	6.2 ± 0.2	2.3 ± 0.1[44,c] 3.7 ± 1.1[22,e] 2.7 ± 0.08[15,e]	440 ± 30	391 ± 25[44,c] 660 ± 210[22,e] 416 ± 12[15,e]
butylbenzene	280 ± 2	286 ± 2[22,e] 296[25,e]	8.2 ± 0.3	6.6 ± 0.5[22,e] 1.29[25,e]	470 ± 50	540 ± 90[22,e] 645[25,e]

[a] The uncertainty shown is the standard deviation calculated from the error propagation law or quoted by the authors. [b] From the recommended fit of γ_1^∞. [c] From calorimetric measurement of $\Delta_{sol}H_1^\infty(T)$. [d] From calorimetric measurement of $\Delta_{sol}C_{p,1}^\infty(T)$, value at 298.15 K. [e] From measurement of $x_1^{sol}(T)$.

solubility measurements of Sanemasa et al.,[2] and gas–liquid partitioning measurements of Robbins et al.[24] carried out by the headspace analysis technique. Similar excellent agreement is noted with static solubility measurements of Sawamura et al.[15] at temperatures >288 K; however, at temperatures <288 K γ_1^∞ values from the measurements of Sawamura et al. are lower (solubilities higher) than our results, the deviation progressively increasing at lower temperatures and reaching at 273 K ~10%. Solubility measurements of Owens et al.[22] by the generator column technique and gas–liquid partitioning measurements of Brown and Wasik,[20] originating from the same laboratory, are all displaced toward lower values of γ_1^∞ (higher solubilities), diverging again from our values at lower temperatures. Solubility measurements of Chen and Wagner[25] at higher temperatures (that appear to cross the trends of other data at ~328–333 K) and many single measurements at ambient temperature (that are almost uniformly scattered) are of little help for resolving the observed discrepancy.

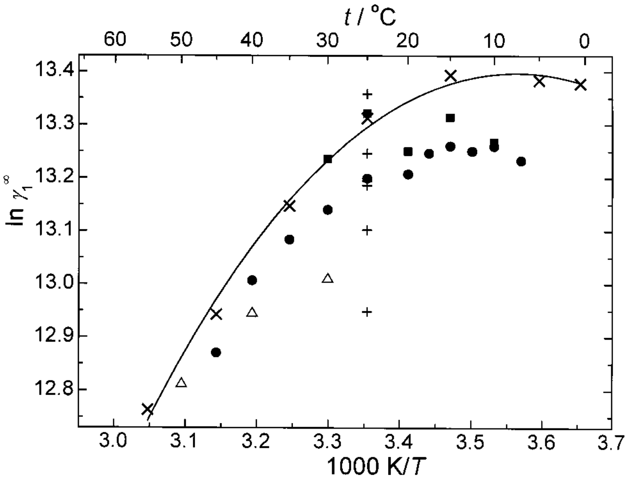

Figure 6. Limiting activity coefficient γ_1^∞ of butylbenzene (1) in water (2) as a function of temperature: ×, this work, SVA; —, fit as given in Table 2 of experimental data from this work; ●, Owens et al.;[22] ■, Perlinger et al.;[23] △, Chen and Wagner;[25] +, single points at 298.15 K from refs 4, 29, 31, 32, 36, 38, and 43.

For propylbenzene in water, as seen from Figure 5, the available data are less abundant. Although at higher temperatures our measurements and all literature data agree reasonably well, at ambient and subambient temperatures our measurements yield appreciably higher values of γ_1^∞ than solubility measurements by the generator column technique (DeVoe et al.[42] and Owens et al.,[22] both from the same laboratory) or by static equilibration (Sawamura et al.[15]). On the other hand, there is a quite good agreement between our results and the SVA solubility measurements of Sanemasa et al.[2] in the temperature range that both of these measurements have in common.

The situation for butylbenzene in water is shown in Figure 6. Just a few measurements are available in the literature for comparison. Similarly to propylbenzene in water, at higher temperatures the present SVA measurements agree satisfactorily with those of Owens et al.[22] and Chen and Wagner,[25] and as the temperature drops the values of γ_1^∞ by Owens et al. are systematically lower. The only other measurement of temperature dependence due to Perlinger et al.[23] is irresolute, favoring at 298 K and 303 K our results, but at favoring at 293 K, 288 K, and 283 K favoring the results of Owens et al.[22]

Table 3 gives some properties derived from the measured temperature dependences of aqueous solubility, namely, the temperature T_{max} at which γ_1^∞ is maximum and caloric properties, enthalpy of solution $\Delta_{sol}H_1^\infty$ at $T_0 = 298.15$ K and heat capacity of solution $\Delta_{sol}C_{p,1}^\infty$, the latter being calculated by standard thermodynamic procedures from eq 2, that is, $\Delta_{sol}H_1^\infty = -RT^2\ \partial \ln \gamma_1^\infty/\partial T$ and $\Delta_{sol}C_p^\infty = \partial\Delta_{sol}H_1^\infty/\partial T$. For comparison, listed in Table 3 are also results obtained from literature measurements, including unique calorimetric ones. The difference between individual results often exceeds significantly their combined uncertainty, causing the mutual agreement to be of rather semiquantitative character. Nevertheless, if one takes into account the great susceptibility of these quantities to experimental error, this situation is comprehensible.

Besides the detailed comparison of data for individual alkylbenzenes as presented above, their homologous trend behavior has been examined, too. Figure 7 shows for two temperatures (298 and 318 K) the variation of limiting activity coefficient of alkylbenzenes in water with the number of carbon atoms of their alkyl chain n_C. The data plotted in Figure 7 are those obtained by the SVA method in this work supplemented for pentylbenzene and hexylbenzene by the data of Owens at al.[22] Within the large scale of this figure ln γ_1^∞ versus n_C appears to be linear with the values of the slope of 1.39 and 1.34 at 298 K and 318 K,

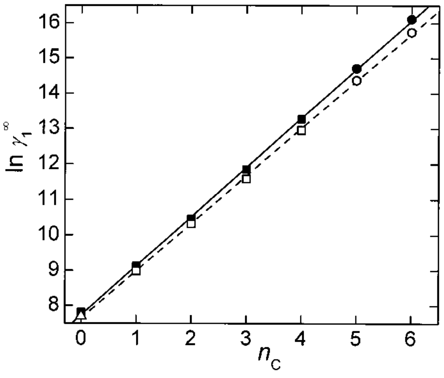

Figure 7. Limiting activity coefficients γ_1^∞ of alkylbenzene (1) in water (2) as a function of the number of carbon atoms of their alkyl chain, n_C: ■, this work, 298.15 K; □, this work, 318.15 K; ●, Owens et al.,[22] 298.15 K; ○, Owens et al.,[22] 318.15 K; △, Hovorka et al.,[16] 318.15 K; — and - - -, straight line fits at 298.15 K and 318.15 K, respectively.

respectively. A closer inspection, however, shows that the methylene increment slightly but continuously increases with n_C.

It is concluded that the SVA technique provides a suitable alternative to conventional liquid−liquid batch contacting for the measurement of the aqueous solubility of volatile organic compounds. The present implementation of the SVA method is faster, completely avoids aggregate formation, and minimizes solute losses due to adsorption and sample manipulation. As a hybrid method, it shares some advantages of techniques for gas−liquid partitioning measurement, yet it does not require exact knowledge of pure solute vapor pressure to obtain the solubility or γ_1^∞. Aqueous solubilities of lower alkylbenzenes (toluene, ethylbenzene, propylbenzene, and butylbenzene) determined with the method in the temperature range from 273 K to 328 K show good reproducibility and precision. For toluene, the results are in excellent agreement with recently recommended data. For ethylbenzene, propylbenzene, and butylbenzene a good agreement with literature data is regularly observed only at higher temperatures; otherwise, the experimental data from different sources are often quite different, with the discrepancy in values being appreciably larger than the quoted precision. Hardly any definitive conclusion can be drawn from their comparison and for a recommendation as accurate as that recently presented for toluene, more experimental effort is still required.

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Received for review June 13, 2001. Accepted August 9, 2001. This work was funded by the MSM 2234 00008 grant from the Ministry of Education of the Czech Republic.

JE010172R