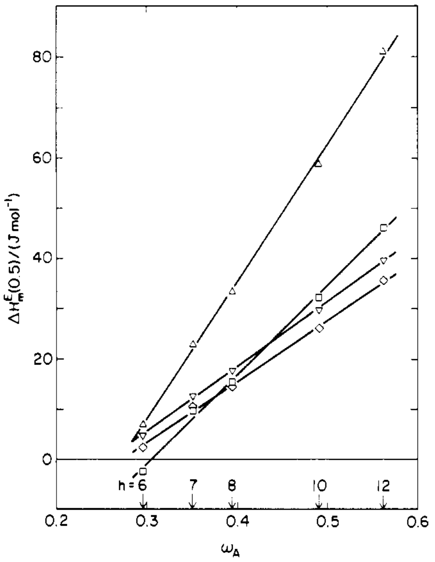

Figure 3. Difference, $\Delta H^E_m(0.5)$, between the excess molar enthalpies at 298.15 K for equimolar binary mixtures of n-alkanes C_hH_{2h+2} (h = 6, 7, 8, 10, 12) with hexane isomers and of the same n-alkanes with n-C6, plotted against the acentric factor, ω_A, of the n-alkane: (▽) 2-MP; (◇) 3-MP; (△) 2,2-DMB; (□) 2,3-DMB (see Figure 2 for sources of the enthalpy data).

increases. For h = 6, 7, 8, and 12 it was noted (1, 2) that the excess molar enthalpies H^E_m (0.5) of equimolar mixtures exhibit a parallel (although nonlinear) behavior when plotted against the molar energies of vaporization ΔE^v_m of the isomers at 298.15 K, as calculated from their molar enthalpies of vaporization (8). Figure 2 shows that the points for the present mixtures with n-decane (h = 10) follow a similar behavioral pattern.

In Figure 3 $\Delta H^E_m(0.5)$, defined as the difference between $H^E_m(0.5)$ for an equimolar mixture of an n-alkane with a hexane isomer (1-3, 9, 10) and $H^E_m(0.5)$ for an equimolar mixture of the same n-alkane with n-C6, is plotted against the acentric factor ω_A of the n-alkane (11). The nearly linear variation observed previously (2) is still evident after the addition of the points representing the present results. The line for 2,3-DMB crosses those for 2-MP and 3-MP, illustrating the shifting relative behavior mentioned above.

Glossary

ΔE^v_m	molar energy of vaporization (of hexane isomer), kJ mol^{-1}
h_i	coefficient in eq 1
H^E_m	excess molar enthalpy, J mol^{-1}
s	standard deviation for least-squares fit of H^E_m, J mol^{-1}
x	mole fraction of n-alkane
ω_A	acentric factor of n-alkane

Registry No. n-C$_6$, 110-54-3; 2-MP, 107-83-5; 3-MP, 96-14-0; 2,2-DMB, 75-83-2; 2,3-DMB, 79-29-8; n-decane, 124-18-5.

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Aqueous Solubilities and Enthalpies of Solution of n-Alkylbenzenes

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Aqueous solubilities of a homologous series of five liquid n-alkylbenzenes, ethylbenzene through n-hexylbenzene, were measured in the range 7-45 °C with an automated coupled-column liquid chromatographic apparatus. Standard molar free energies, enthalpies, and heat capacity changes for the solution process were evaluated by the least-squares method of Clarke and Glew and combined with published vaporization data in order to calculate the corresponding quantities for the hydration process (g → aq). The methylene increments for free energy, enthalpy, and entropy of hydration in this series are close to those that have been determined for n-alkanes.

Introduction

Low-molecular-weight n-alkylbenzenes are hydrophobic liquids that are useful for studying the effects of alkyl chain length on the thermodynamics of the aqueous solution process. The aqueous solubilities of these compounds are conveniently measured by a coupled-column liquid chromatographic method (1, 2), with the benzene moiety providing the chromophore required for UV detection. The solubilities are so low that saturated solutions are nearly ideal dilute solutions; thus accurate enthalpies and entropies of solution can in principle be obtained from the temperature dependence of the solubility. The solubility data can be combined with vaporization data available in the literature in order to calculate thermodynamic properties of the gas-to-water transfer process which is of fundamental importance in understanding hydrophobic interactions.

The aqueous solubilities of benzene and the lower n-alkylbenzenes each display a minimum near room temperature (3).

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This interesting property is a thermodynamic consequence of a reversal in sign of the enthalpy of solution, from negative at temperatures below the minimum to positive above. The sign reversal has been confirmed by direct calorimetry (*4*). Thus the partial molar heat capacity change for solution, ΔC_p, is large and positive for these solutes in agreement with those theories that explain hydrophobic effects by a structuring of water around the dissolved solute molecule (*5*).

This paper describes aqueous solubility measurements for the five members of the homologous series ethylbenzene through *n*-hexylbenzene made at various temperatures in the range 7–45 °C by means of an automated coupled-column liquid chromatographic apparatus, and the evaluation from these data of thermodynamic quantities for the liq → aq and g → aq processes.

Experimental Section

Ethylbenzene was obtained from Aldrich Chemicals and the other *n*-alkylbenzenes from Albany International Chemicals Division. (Certain trade names and company products are identified in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the products are necessarily the best available for the purpose.) The purity of each of these derivatives was checked by GC and found to be at least 99%. The water and methanol were HPLC grade.

Aqueous solubilities were measured by a coupled-column liquid chromatographic technique using an automated apparatus. The technique was originally developed by May et al. to measure aqueous solubilities of solid polycyclic aromatic hydrocarbons (*1*) and was later extended to liquid solutes (*2*). The technique minimizes or avoids several experimental problems inherent in the usual "shake-flask" method: formation of colloidal dispersions, errors from adsorption on internal surfaces, and loss of solute to the atmosphere. With this technique, a saturated solution of the organic solute was generated by pumping water through a thermostated generator column containing the solute coated on a chromatographic support (Chromosorb W). A known volume of the saturated solution was passed through a small extractor column filled with reverse phase packing where the solute was removed quantitatively. The extracted solute was then eluted from the extractor column with a water–methanol mixture, separated from impurities on an HPLC analytical column, and analyzed by UV detection at 254 nm.

Each integrated peak area was multiplied by a response factor in order to determine the amount of solute in the known volume of solution and thus the solute concentration in the saturated solution. The response factor was determined for each solute by injecting solutions of known concentration into the HPLC column using a 50-μL sample loop whose volume had been determined to ±1% by a spectrophotometric method (*2*). The standard deviation of the peak area for the known solution of any one solute was 2.4% or less.

In the automated apparatus, a microcomputer controlled the timed operations and prescheduled temperature changes for measurements on each solute. The temperature during each measurement was constant to within 0.05 °C. The apparatus is described in detail elsewhere (*6*).

Results and Discussion

Table I lists the main values and standard deviations of the solubility measurements for each solute at various temperatures.

Table I. Aqueous Solubilities of Alkylbenzenes Measured by the Coupled-Column Liquid Chromatographic Method at Various Temperatures

temp, °C	solubility[a]	*n*[b]
	Ethylbenzene (10^{-3} M)	
10.0	1.850 ± 0.084	6
14.0	1.812 ± 0.050	4
17.0	1.776 ± 0.061	3
18.0	1.725 ± 0.013	5
19.0	1.676 ± 0.064	5
20.0	1.770 ± 0.032	5
21.0	1.724 ± 0.030	7
22.0	1.713 ± 0.072	4
23.5	1.751 ± 0.088	4
25.0	1.811 ± 0.028	4
25.8	1.753 ± 0.037	10
28.0	1.747 ± 0.038	8
30.0	1.777 ± 0.103	5
35.0	1.818 ± 0.051	4
40.0	1.928 ± 0.060	6
45.0	1.991 ± 0.053	7
	n-Propylbenzene (10^{-4} M)	
10.0	4.47 ± 0.15	4
15.0	4.35 ± 0.12	4
20.0	4.52 ± 0.11	2
25.0	4.43 ± 0.10	5
30.0	4.37 ± 0.16	5
35.0	4.71 ± 0.30	4
40.0	5.32 ± 0.27	4
45.0	5.54 ± 0.12	3
	n-Butylbenzene (10^{-4} M)	
7.0	0.994 ± 0.029	4
10.0	0.967 ± 0.010	7
12.5	0.979 ± 0.013	4
15.0	0.966 ± 0.020	4
17.5	0.979 ± 0.012	4
20.0	1.018 ± 0.023	4
25.0	1.025 ± 0.041	4
30.0	1.086 ± 0.013	4
35.0	1.147 ± 0.036	3
40.0	1.234 ± 0.033	4
45.0	1.411 ± 0.009	3
	n-Pentylbenzene (10^{-5} M)	
7.0	2.348 ± 0.131	4
10.0	2.144 ± 0.278	5
12.5	2.323 ± 0.147	4
15.0	2.153 ± 0.005	2
17.5	2.311 ± 0.083	4
20.0	2.142 ± 0.053	4
25.0	2.276 ± 0.102	3
30.0	2.433 ± 0.042	4
35.0	2.642 ± 0.045	6
40.0	2.868 ± 0.030	4
45.0	3.163 ± 0.053	4
	n-Hexylbenzene (10^{-6} M)	
7.0	5.14 ± 0.15	3
10.0	5.15 ± 0.24	3
15.0	5.09 ± 0.24	2
20.0	5.86 ± 0.18	3
25.0	5.56 ± 0.11	3
30.0	6.14 ± 0.34	3
35.0	6.59 ± 0.15	3
40.0	6.59 ± 0.55	2
45.0	8.00 ± 0.23	2

[a] Mean and standard deviation, in the units shown next to the compound name. [b] Number of measurements.

In order to describe the solubilities as functions of temperature, we converted each solubility value s in molarity units to solute mole fraction X_s by using $X_s = Ms/d$ where M is the molar mass of water and d is the density of water at the temperature of the measurement. For each solute, the values of $R \ln X_s$ (where R is the gas constant) were then fitted by multiple linear least-squares regression to the function of absolute temperature T recommended by Clarke and Glew (*7*):

$$R \ln X_s = -\Delta G^\circ_\theta/\theta + \Delta H^\circ_\theta(1/\theta - 1/T) + \Delta C_p{}^\circ_\theta[\theta/T - 1 - \ln(\theta/T)] \quad (1)$$

Table II. Aqueous Solubilities of Alkylbenzenes at 25 °C

compd	solubility, mM this work[a]	 lit.
ethylbenzene	1.74 ± 0.02 (n = 87)	1.23 (*8*), 1.43 (*9*), 1.514 (*10*), 1.54 (*11*), 1.58 (*12*), 1.59 (*13*), 1.64 (*14*), 1.66 (*15*), 1.76 (*16*), 1.96 (*3*), 2.00 (*17*)
n-propylbenzene	0.437 ± 0.010 (n = 31)	0.423 (*13*), 0.432 (*2*), 0.434 (*16*), 0.46 (*12*), 0.499 (*18*), 0.552 (*17*), 1.1 (*14*)
n-butylbenzene	0.103 ± 0.001 (n = 45)	0.094 (*12*), 0.103 (*16*), 0.111 (*10*), 0.132 (*19*), 0.242 (*17*), 0.37 (*14*)
n-pentylbenzene	0.0230 ± 0.0007 (n = 44)	0.0259 (*16*), 0.13 (*17*)
n-hexylbenzene	0.0057 ± 0.0002 (n = 24)	0.00613 (*20*), 0.00627 (*16*), 0.106 (*17*)

[a] Fitted with eq 1. 95% confidence limits are shown. n is the number of measurements used in the fit.

The precision of our data did not justify including additional terms that are given by Clarke and Glew. The most important contribution to experimental imprecision was probably the integration of peak areas, as illustrated by the standard deviations (2.4% or less) of the peak areas obtained in measuring response factors. All X_s values of a solute were assumed to be subject to the same relative error, and therefore the values of $R \ln X_s$ were not weighted in the regression analyses.

Each regression analysis yielded best estimates and standard errors of the parameters (eq 1) ΔG°_θ, ΔH°_θ, and $\Delta C_p{}^\circ_\theta$, which are the standard molar free energy, enthalpy, and heat capacity change, respectively, for the solution process at a reference temperature θ. The parameters were evaluated with θ set equal to 298.15 K. In addition, the standard error of ΔG°_θ was obtained at other temperatures by repeating the analyses with other values of θ and used to evaluate the 95% confidence intervals of $\ln X_s$ at these temperatures through the relation $\ln X_s(\theta) = \Delta G^\circ_\theta / R$.

Figure 1 shows the temperature dependencies of the solubilities obtained from our regression analyses. The best estimates of the solubilities (solid curves) are plotted as $\ln X_s$ vs. temperature. Each set of dashed curves encloses the 95% confidence interval of $\ln X_s$ obtained from the standard errors of ΔG°_θ at different temperatures. The existence of a solubility minimum is evident for the first four solutes, and the trend for the temperature of the minimum is seen to be downward with increasing chain length.

Table II lists the aqueous solubilities ($s = X_s d/M$) and their uncertainties at 25 °C derived from the regression analyses. Values of solubilities from the literature (*2*, *3*, *8*-*20*) are given for comparison. There is a considerable spread in the literature solubilities for each solute, the ratio of highest value to lowest value increasing from 1.6 for ethylbenzene to 17 for n-hexylbenzene. The solubilities at 25 °C determined in the present work are within 11% of values previously measured by the coupled-column liquid chromatographic method (*16*, *20*).

Table III shows the enthalpies and heat capacity changes for the solution process at 25 °C, as well as temperatures of minimum solubility calculated from $T^* = \theta - \Delta H^\circ_\theta / \Delta C_p{}^\circ_\theta$. The ΔH and ΔC_p values from our data agree within experimental error with those obtained by Bohon and Claussen (*3*) and by May et al. (*20*) from the temperature dependencies of the solubilities measured by them. The values of ΔH and ΔC_p obtained calorimetrically by Gill et al. (*4*) fall slightly outside the 95% confidence intervals of our values.

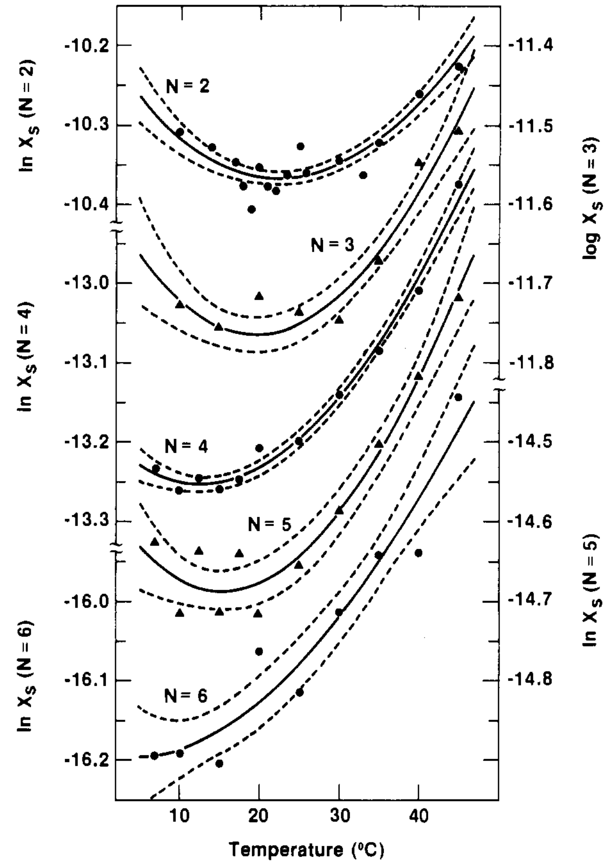

Figure 1. In X_s as a function of temperature for five n-alkylbenzenes. Solid curves: best estimates of the functions from fit of eq 1 to solubility measurements; dashed curves: 95% confidence limits; circles and triangles: mean of two or more measurements at the same temperature.

The value of any thermodynamic quantity for the solution process is influenced by both solute-solute interactions in the liquid solute phase and solute-water interactions in the aqueous phase. When it is the solute-water interactions that we wish to study, omitting solute-solute interactions, the appropriate process to consider is hydration (g → aq). Any hydration quantity ΔX (where X is free energy, enthalpy, etc.) may be calculated as the difference of the solution and vaporization quantities: $\Delta X(\text{g} \rightarrow \text{aq}) = \Delta X(\text{liq} \rightarrow \text{aq}) - \Delta X(\text{liq} \rightarrow \text{g})$.

Table IV lists values calculated in this way of the standard molar free energies, enthalpies, entropies, and heat capacity changes of hydration at 25 °C for the series benzene through n-hexylbenzene. The solution quantities used to obtain these

Table III. Enthalpies and Heat Capacities of Solution at 25 °C, and Temperatures of Minimum Solubility

compd	ΔH_{soln}, kJ mol^{-1} this work[a]	 lit.	ΔC_p, kJ K^{-1} mol^{-1} this work[a]	 lit.	t^*,[a] °C
ethylbenzene	1.3 ± 0.6	1.6 (*3*) 2.02 ± 0.04[b] (*4*)	0.47 ± 0.10	0.45 (*3*) 0.32 ± 0.01[b] (*4*)	22 ± 2
n-propylbenzene	3.7 ± 1.1	2.3 ± 0.1[b] (*4*)	0.66 ± 0.21	0.39 ± 0.03[b] (*4*)	19 ± 3
n-butylbenzene	6.6 ± 0.5		0.54 ± 0.09		13 ± 2
n-pentylbenzene	6.5 ± 1.1		0.67 ± 0.22		15 ± 4
n-hexylbenzene	8.0 ± 1.4	7.6 ± 1.4[a] (*20*)	0.38 ± 0.26	0.51 ± 0.16[a] (*20*)	4 ± 14

[a] 95% confidence limits are shown. [b] The uncertainty shown is twice the standard deviation.

Table IV. Thermodynamic Parameters for the Process g → aq at 25 °C[a]

	ΔG°, kJ mol^{-1}	ΔH°, kJ mol^{-1}	ΔS°, kJ K^{-1} mol^{-1}	ΔC_p°, kJ K^{-1} mol^{-1}
benzene[b]	−3.63 ± 0.01	−31.89 ± 0.18	−0.0948 ± 0.0006	0.30 ± 0.02
toluene[b]	−3.70 ± 0.01	−36.18 ± 0.20	−0.1089 ± 0.0007	0.35 ± 0.02
ethylbenzene[b]	−3.31 ± 0.02	−40.10 ± 0.38	−0.1234 ± 0.0013	0.33 ± 0.04
ethylbenzene[c]	−3.02 ± 0.02	−40.94 ± 0.62	−0.1271 ± 0.0021	0.52 ± 0.10
n-propylbenzene[c]	−2.14 ± 0.06	−42.53 ± 1.10	−0.1354 ± 0.0037	0.72 ± 0.21
n-butylbenzene[c]	−1.42 ± 0.03	−44.15 ± 0.45	−0.1433 ± 0.0015	0.61 ± 0.09
n-pentylbenzene[c]	−0.67 ± 0.07	−49.47 ± 1.11	−0.1636 ± 0.0037	0.76 ± 0.22
n-hexylbenzene[c]	−0.05 ± 0.08	−52.34 ± 1.39	−0.1754 ± 0.0047	0.48 ± 0.26
n-hexylbenzene[d]	−0.21 ± 0.02	−52.7 ± 1.4	−0.176 ± 0.005	0.61 ± 0.16

[a] The standard states for gas and solution are on a concentration basis. The uncertainties are the 95% confidence limits of the liq → gas process. [b] Values obtained from ref *21*, corrected for changes in the standard state convention. [c] Solubility data from the present work, vaporization data from ref *22*. [d] Solubility data fitted in ref *20* to eq 1, vaporization data from ref *22*.

Table V. Parameters of the Equation $\Delta X^\circ = a + bN$ for the Process liq → aq at 25 °C[a]

		toluene through *n*-hexylbenzene[b]			b[c]
ΔX°	units	a[c]	b[c]	r[d]	(Abraham (*23*))
ΔG°	kJ mol^{-1}	−4.46 ± 0.03	0.749 ± 0.015	0.9992	0.611 ± 0.013[e]
ΔH°	kJ mol^{-1}	−33.3 ± 0.6	−2.93 ± 0.25	0.9853	−3.2[f]
ΔS°	J K^{-1} mol^{-1}	−96.9 ± 1.8	−12.4 ± 0.8	0.9912	−13[g]

[a] N is the number of carbon atoms in the side chain. The standard states for gas and solution are on a concentration basis. [b] Data from Table IV. The values of ΔX° for toluene from ref *21* and for the series ethylbenzene through *n*-hexylbenzene from the present work were fitted to a linear function of N by using weighted least squares. The weight of each point was set equal to the reciprocal of the 95% confidence interval squared. [c] The uncertainties shown are standard errors. [d] Correlation coefficient. [e] Based on solubilities of the series toluene through *n*-hexylbenzene (*16*, *24*). [f] Based on calorimetric enthalpies of solution of the series toluene through *n*-propylbenzene (*4*), and the temperature dependence of the solubility of *n*-hexylbenzene (*20*). [g] Toluene through *n*-propylbenzene, and *n*-hexylbenzene.

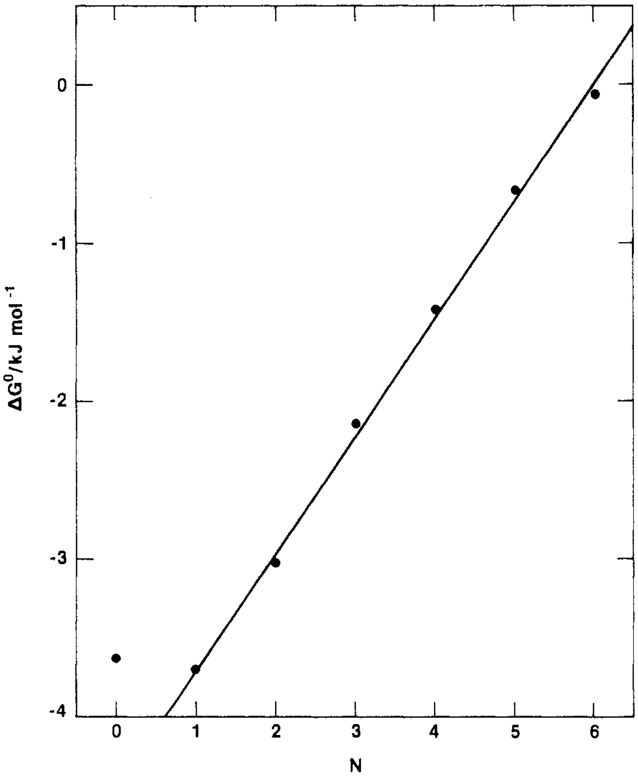

Figure 2. ΔG° for the process g → aq at 25 °C as a function of alkyl chain length N. The line was obtained from weighted least-squares regression of points for the series N = 1–6 (see Table V).

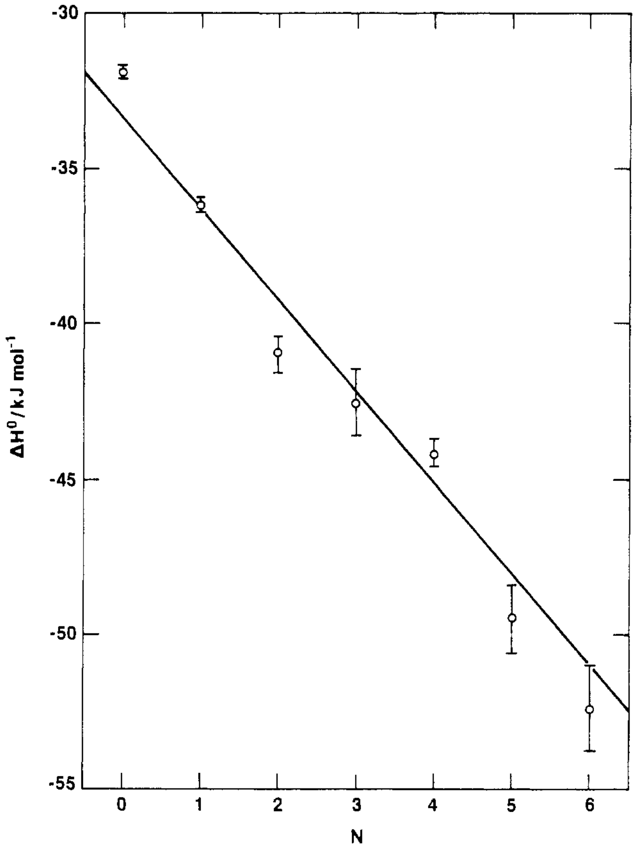

Figure 3. ΔH° for the process g → aq at 25 °C as a function of alkyl chain length N. The line was obtained from weighted least-squares regression of points for the series N = 1–6 (see Table V). The error bars are the 95% confidence intervals of ΔH°.

hydration values are from the present work, May et al. (*20*), and Wauchope and Haque (*21*), derived in each case from solubility measurements over a range of temperatures by the least-squares method of Clarke and Glew (*7*). Wauchope and Haque (*21*) report hydration quantities without stating the source of the vaporization data; for the other hydration quantities in Table IV the vaporization quantities were obtained from Antoine constants for the solutes given by Dreisbach (*22*). The quantities are calculated for standard states on a concentration basis (equal solute concentrations approaching infinite dilution in gas and aqueous phases); with this choice of standard states the contributions from solute translational entropies in both phases cancel. The values obtained from the present work are close to those derived from the data of the other workers in those cases where comparisons are possible (ethylbenzene and *n*-hexylbenzene).

Abraham (*23*) recently investigated data for the hydration process in several homologous series, including *n*-alkylbenzenes. He documented the existence of linear relations between the standard molar free energies, enthalpies, and entropies of hydration and the number of carbon atoms, and concluded that methylene increments for the free energies and enthalpies vary among series. Figures 2 and 3 show that our free energy and enthalpy values for the series ethylbenzene through *n*-hexylbenzene combined with literature values (*21*) for toluene display these linear relations within experimental error. The points for benzene, however, lie off the lines as might be expected from an end effect in the series. From regression of the data for toluene through *n*-hexylbenzene against chain length *N* we obtained the intercepts *a* and methylene increments (slopes) *b* listed in Table V. The table also lists methylene increments obtained by Abraham (*23*) using other data. Our value for the methylene increment of the free energy of hydration in *n*-alkylbenzenes (0.75 kJ mol^{-1}) is 23% higher than that obtained by Abraham, but is close to the value (0.74 kJ mol^{-1}) which he calculated for the methylene increment in lower members of the *n*-alkane series (ethane through *n*-octane). Our values for the methylene increments of enthalpy and entropy also agree within experimental uncertainty with those given by Abraham for both *n*-alkylbenzenes (Table V) and alkanes. Thus Abraham's conclusion that methylene increments differ from one homologous series to another may be premature, since the values of these increments are sensitive to the accuracy of the solubility data.

Registry No. Ethylbenzene, 100-41-4; *n*-propylbenzene, 103-65-1; *n*-butylbenzene, 104-51-8; *n*-pentylbenzene, 538-68-1; *n*-hexylbenzene, 1077-16-3.

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Henry Constant of Molecular Chlorine in Aqueous Solution

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The gas–liquid phase equilibrium for molecular chlorine absorbing into aqueous solution was measured directly under conditions (pH $\simeq$ 1) such that only minimal corrections were necessary to adjust for chlorine hydrolysis. The Henry constant for Cl_2 at 20 °C and zero ionic strength was observed to be 13.57 atm·L·mol^{-1}. The Henry constant was approximately twice as great at 30 °C as at 10 °C, corresponding to an enthalpy of dissolution of 26.7 kJ·mol^{-1}. The Henry constant increased with increasing NaCl concentration, in a manner consistent with the salting-out effect. However, increasing the concentration of HCl in solution caused the opposite effect: the chlorine solubility increased, resulting in a decrease of the Henry constant for Cl_2.

Introduction

Accurate data on the air–water phase equilibrium of molecular chlorine has important applications in water treatment in the design of chlorine supply systems (*1*) and of chlorine dioxide generators (*2*, *3*). In supplying chlorine for water treatment, molecular chlorine often is used in gaseous form and must be transferred from the gas phase into aqueous solution. Accurate knowledge of the equilibrium concentration of molecular chlorine at the air–water interface is essential to calculate the mass-transfer driving force.

It is important to distinguish between molecular chlorine solubility (i.e., the inverse of the Henry constant for Cl_2, in appropriate units) and total chlorine solubility. Dissolved molecular chlorine in aqueous solution rapidly undergoes hydrolysis to form hypochlorous acid, thus increasing the solubility to values exceeding that of molecular chlorine. Previous researchers (*4*, *5*) have estimated the Henry constant of Cl_2 by correcting total chlorine solubility data (the sum of molecular chlorine, hypochlorous acid, and hypochlorite ion) to adjust for the effect of chlorine hydrolysis. In order to determine the Henry constant for chlorine from such data, the chlorine hydrolysis equilibrium constant, the final solution pH, and the final chloride ion concentration must be known accurately. However, compilations of chlorine solubility given in widely used handbooks (*1*, *6*) lack some of the information on conditions (pH, chloride concentration) needed to infer values of the Henry constant for molecular chlorine. In this study, the liquid-phase molecular chlorine concentration was determined directly, obviating the

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