Table III. Calculated Constants for Eq 1-3

a, K	12968 ± 95	d	0.2927 ± 0.0009
b	−11.058 ± 0.312	x, K	1379.33 ± 6.43
c, K	27.066 ± 0.240	y	−11.014 ± 0.012

all three solvents are probably best considered to be normal polar liquids.

Acknowledgment

We are grateful to Dr. Allan H. Fawcett of the Department of Chemistry, The Queen's University of Belfast, Northern Ireland, for providing the facilities for measuring relative permittivities and conductivities.

Glossary

a, b	constants in eq 1, a has units of K
c, d	constants in eq 2, c has units of K
x, y	constants in eq 3, x has units of K
g	Kirkwood correlation factor
k	Boltzmann constant, J K^{-1}
k_{diff}	diffusion-controlled rate constant, dm^3 mol^{-1} s^{-1}
n_D	refractive index
A	Arrhenius A factor, dm^3 mol^{-1} s^{-1}
E_{act}	activation energy, kJ mol^{-1}
E_{vis}	activation energy of viscous flow, kJ mol^{-1}
M	molar mass, kg mol^{-1}
N	Avogadro number, mol^{-1}
R	gas constant, J mol^{-1} K^{-1}
T	temperature, K
ϵ_r	relative permittivity
ϵ_∞	high-frequency relative permittivity (= 1.1 × n_D^2)
ϵ_0	permittivity of vacuum, C^2 N^{-1} m^{-2}
η	viscosity, N s m^{-2}
μ_0	dipole moment, C m
ρ	density, kg m^{-3}

Conductivity is in units of S m^{-1} (1 siemen = 1 mho)

Registry No. NMP, 872-50-4.

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Received for review September 22, 1986. Accepted June 30, 1987.

Enthalpies of Solution of Butanes in Water from 5 to 45 °C

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The enthalpies of solution of *n*-butane and isobutane (2-methylpropane) have been determined by direct calorimetry over a range of 0–45 °C. The temperature dependence of the enthalpies of solution allows accurate determination of the heat capacity change for the solution process as a function of temperature. A simple two-energy-state model of water molecules in the first solvation shell, developed to account for the heat capacity properties of small hydrocarbons in solution, has been found to predict the heat capacity changes upon solution for *n*-butane and isobutane as well.

Introduction

In previous papers, an extensive study of the heats of solution of methane (*1*) and ethane and propane (*2*) over as wide a temperature range as is currently experimentally practical was made. This work has now been extended to *n*-butane and isobutane with the purpose of obtaining precise energetic data about larger gaseous hydrocarbon solutes by direct calorimetry, in order that a critical comparison with van't Hoff studies (*3*) can be made. These results have also been of great value in further testing the generality of the simple two-state model of water molecules in the first solvation shell, which predicts, for hydrophobic solutes, abnormally large values for the heat capacities, which decrease with increasing temperature. The theoretical basis of the model and its application to other compounds are discussed in detail elsewhere (*1*, *2*, *4*).

Table I. Enthalpy of Solution of *n*-Butane in Water from 0 to 45 °C

temp, K	$\Delta H°$ ± 2σ, kJ mol^{-1}	no. of determinations
273.25	−35.68 ± 0.22	3
278.15	−33.62 ± 0.43	5
283.15	−31.60 ± 0.31	5
288.15	−29.26 ± 0.18	5
293.15	−27.38 ± 0.34	4
298.15[a]	−25.92 ± 0.17	11
303.15	−23.67 ± 0.17	4
308.15	−22.15 ± 0.17	6
313.15	−20.15 ± 0.17	5
318.15	−17.81 ± 0.15	4

[a] Reference *13*.

Experimental Section

The microcalorimeter and its method of operation have been described previously (*5*). *n*-Butane (Scientific Gas Products)

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0021-9568/87/1732-0422$01.50/0

Table II. Enthalpy of Solution of Gaseous Isobutane (2-Methylpropane) in Water from 0 to 35 °C

temp, K	$\Delta H^\circ \pm 2\sigma$, kJ mol^{-1}	no. of determinations
273.24	-33.10 ± 0.35	4
278.15	-31.24 ± 0.15	4
283.15	-29.90 ± 0.09	4
288.15	-27.18 ± 0.37	3
293.15	-25.42 ± 0.24	3
298.15[a]	-24.11 ± 0.25	7
303.15	-22.28 ± 0.21	4
308.15	-20.33 ± 0.67	4

[a] Reference *13*.

Table III. Comparison of Calorimetric and van't Hoff Enthalpies of Solution (kJ mol^{-1}) of Gaseous *n*-Butane in Water at Different Temperatures

	calorimetric		van't Hoff
T, K	$\Delta H^{\circ a}$	$\Delta H^{\circ b}$	$\Delta H^{\circ c}$
273.15	-35.49 ± 0.31		-35.3
278.15	-33.49 ± 0.20		-33.4
283.15	-31.52 ± 0.15		-31.6
288.15	-29.56 ± 0.14	-29.71 ± 0.22	-29.7
293.15	-27.61 ± 0.15		-27.8
298.15	-25.70 ± 0.15	-25.93 ± 0.08	-26.0
303.15	-23.78 ± 0.14		-24.1
308.15	-21.89 ± 0.14	-21.23 ± 0.06	-22.2
313.15	-20.02 ± 0.19		-20.4
318.15	-18.16 ± 0.29		-18.5

[a] This work. Uncertainty is twice the standard deviation as calculated by using an equal temperature interval data set based on eq 1. [b] Olofssen et al. (ref *8*). Uncertainty as reported. [c] Wilhelm et al. (ref *3*). No uncertainty of the enthalpy charge is available from their analysis. However, the percentage standard deviation of the fitted Henry's constant was reported as 7.8, indicative of relatively large errors.

and isobutane (Scientific Gas Products) had specified purities of 99.99% and 99.96%, respectively. The partial pressure of water vapor was calculated from the results of Ambrose and Lawrenson (*6*) and the virial coefficients of *n*-butane and isobutane were obtained from the compilation of Dymond and Smith (*7*). Lower solubility made these gases more difficult to study than determinations for methane, ethane, and propane.

Results and Discussion

From the enthalpy of solution of the hydrocarbon gases at near-atmospheric pressure, values of the standard enthalpy change, ΔH°, for solution of *n*-butane and isobutane into water were determined. The experimental data are summarized in Tables I and II. Errors are reported as twice the standard error (2σ), and the number of experimental determinations at each temperature is given.

The temperature dependence of the enthalpy of solution is represented as a Taylor's series expansion of the enthalpy change and its derivatives as follows:

$$\Delta H^\circ(T) = \Delta H^\circ(\theta) + \Delta C_p{}^\circ(\theta)(T-\theta) + \frac{1}{2}\left(\frac{\mathrm{d}\Delta C_p{}^\circ}{\mathrm{d}T}\right)_\theta (T-\theta)^2 + \ldots \quad (1)$$

Higher order terms reflect the temperature-dependent higher derivatives of the standard-state heat capacity change. A least-squares fit of the data to eq 1 provides the best estimates of the thermodynamic parameters of the system. The ΔH°, $\Delta C_p{}^\circ$, and $(\mathrm{d}\Delta C_p{}^\circ/\mathrm{d}T)$ values for a given temperature are calculated by fitting all data using that temperature equal to θ. The process is illustrated in Figure 1 by the theoretical line determined for *n*-butane (a) and isobutane (b) by a three-parameter fit to eq 1 with a reference temperature of 298.15 K. The inclusion of a fourth term in eq 1 did not improve the fitting to a significant extent. The calculated values of ΔH°, $\Delta C_p{}^\circ$, and $(\mathrm{d}\Delta C_p{}^\circ/\mathrm{d}T)$ for 5 K intervals are summarized in Tables III–VI. Included for comparison are van't Hoff's values (*3*) and earlier calorimetric (*8*) ΔH° and $\Delta C_p{}^\circ$ values.

Table IV. Comparison of Calorimetric and van't Hoff $\Delta C_p{}^\circ$ (J K^{-1} mol^{-1}) and $\mathrm{d}(\Delta C_p{}^\circ)/\mathrm{d}T$ of *n*-Butane in Water at Different Temperatures

	calorimetric[a]		calorimetric[b]	van't Hoff[c]
T, K	$\Delta C_p{}^\circ$	$\mathrm{d}\Delta C_p{}^\circ/\mathrm{d}T$	$\Delta C_p{}^\circ$	$\Delta C_p{}^\circ$
273.15	401 ± 30	-0.35 ± 0.63		373
278.15	397 ± 24	-0.35 ± 0.63		373
283.15	394 ± 18	-0.35 ± 0.63		373
288.15	390 ± 13	-0.35 ± 0.63		373
293.15	387 ± 9	-0.35 ± 0.63	380 ± 25	373
298.15	383 ± 9	-0.35 ± 0.63		373
303.15	380 ± 12	-0.35 ± 0.63	470 ± 10	373
308.15	376 ± 17	-0.35 ± 0.63		373
313.15	373 ± 23	-0.35 ± 0.63		373
318.15	369 ± 29	-0.35 ± 0.63		373

[a] This work. Uncertainty is twice the standard deviation as calculated by using an equal temperature interval data set based on eq 1. [b] Olofsseen et al. (ref *8*). Uncertainty as reported. [c] Wilhelm et al. (ref *3*). No uncertainty estimate is available for this parameter.

Table V. Comparison of Calorimetric and van't Hoff Enthalpies of Solution (kJ Mol^{-1}) of Gaseous Isobutane in Water at Different Temperatures

T, K	calorimetric $\Delta H^{\circ a}$	van't Hoff $\Delta H^{\circ b}$
273.15	-33.18 ± 0.34	-18.9
278.15	-31.31 ± 0.21	-19.6
283.15	-29.45 ± 0.20	-20.3
288.15	-27.60 ± 0.22	-21.0
293.15	-25.78 ± 0.21	-21.8
298.15	-23.97 ± 0.19	-22.5
303.15	-22.18 ± 0.20	-23.2
308.15	-20.41 ± 0.34	-23.9

[a] This work. Uncertainty is twice the standard deviationas calculated by using an equal temperature interval data set based on eq 1. [b] Wilhelm et al. (ref *3*). No uncertainty of the enthalpy change is available from their analysis. However, the percentage standard deviation of the fitted Henry's constant was reportedas 3.1, indicative of relatively large errors.

Table VI. Comparison of Calorimetric and van't Hoff $\Delta C_p{}^\circ$ (J K^{-1} mol^{-1}) and $\mathrm{d}(\Delta C_p{}^\circ)/\mathrm{d}T$ of Isobutane in Water at Different Temperatures

	calorimetric[a]		van't Hoff[b]
T, K	$\Delta C_p{}^\circ$	$\mathrm{d}(\Delta C_p{}^\circ)/\mathrm{d}T$	$\Delta C_p{}^\circ$
273.15	377 ± 46	-0.36 ± 1.27	-144
278.15	374 ± 34	-0.36 ± 1.27	-144
283.15	370 ± 22	-0.36 ± 1.27	-144
288.15	367 ± 12	-0.36 ± 1.27	-144
293.15	363 ± 14	-0.36 ± 1.27	-144
298.15	360 ± 23	-0.36 ± 1.27	-144
303.15	356 ± 34	-0.36 ± 1.27	-144
308.15	352 ± 46	-0.36 ± 1.27	-144

[a] This work. Uncertainty is twice the standard deviation as calculated by using an equal temperature interval data set based on eq 1. [b] Wilhelm et al. (ref *3*). No uncertainty estimate is available for this parameter.

It is apparent that for *n*-butane there is good agreement between the direct calorimetric measurements of ΔH° and the van't Hoff values. However, in the case of isobutane there is a significant deviation both in magnitude and the observed temperature dependence of ΔH°, as compared to the temperature dependence observed for all hydrophobic solutes for which precise data are available. This is also the case for the reported $\Delta C_p{}^\circ$ values. Although their analysis does not permit estimation of the errors present in the calculated thermodynamic quantities, the relatively large errors in the representation

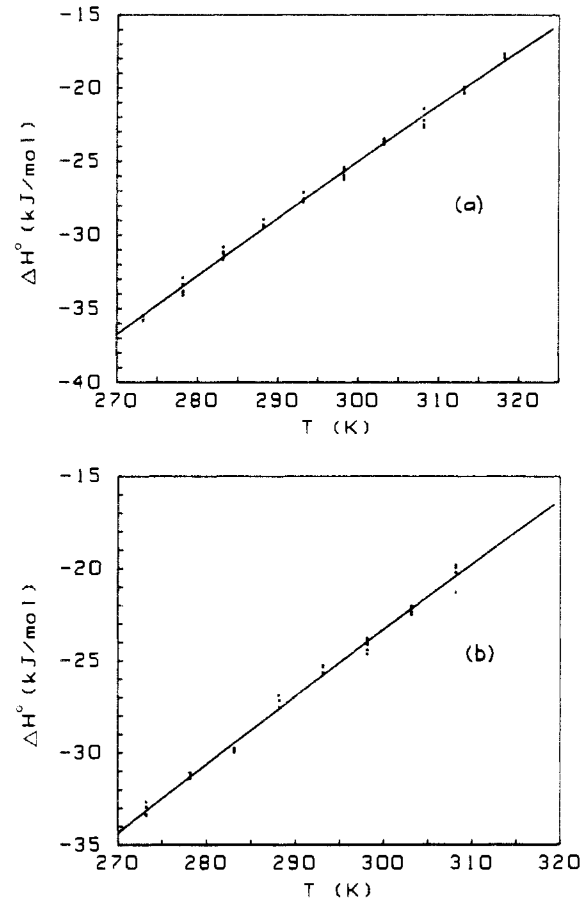

Figure 1. Enthalpy change, ΔH°, as a function of temperature for the solution of (a) *n*-butane and (b) isobutane in water. The range of experimental results at a given temperature are indicated by vertical boxes. The theoretical line was calculated by least-squares analysis of all points using eq 1, θ = 298.15 K.

Table VII. Thermodynamic Functions for Solution of *n*-Butane and Isobutane in Water at 298.15 K

	ΔG°,[a] kJ/mol	$\Delta H^\circ \pm 2\sigma$,[b] kJ/mol	$T\Delta S^\circ$, kJ/mol
butane	26.59	-25.70 ± 0.15	-52.29
isobutane	27.60	-23.97 ± 0.19	-51.57

[a] Wilhelm et al. (ref *3*). No uncertainty estimate is available for this parameter. [b] This work. Uncertainty is twice the standard deviation as calculated by using an equal temperature interval data set bassd on eq 1.

of the solubility data as a function of temperature (*3*) (estimated percentage standard error of 7.8 and 3.1 for *n*-butane and isobutane respectively) lead to the conclusion that any agreement between the direct calorimetric measurements and the van't Hoff's values is probably fortuitous.

Although the analysis of Wilhelm et al. (*3*) does not permit estimation of the probable error in ΔG° of solution, their solubility data have been used, along with the ΔH° values reported here, to evaluate the entropy change upon solution. These values are presented in Table VII. It is apparent that for determination of enthalpy and heat capacity changes the direct calorimetric method is superior to the van't Hoff method using the best available solubility vs. *T* data, allowing a more realistic assessment of the probable error. Extension of very high precision solubility measurements (*9*) to the larger hydrocarbons will, of course, narrow this gap and more importantly allow a precise evaluation of ΔS° of solution.

A prime motivation for determining the enthalpies of solution to a high degree of precision was to evaluate the change in partial molar heat capacity of the hydrocarbons upon solution in water, in order that the simple two-state model for water molecules in the first solvation shell could be further tested. The water molecules in the first solvation shell are pictured as existing in one of two states separated by an energy ΔH_{sh}, determined by whether the water molecule is able to form three or four hydrogen bonds with its neighbors; the energy state of each water molecule is assumed to be independent of the energy states of its neighbors. The excess heat capacity arises from the temperature-dependent equilibrium between the two states, its magnitude determined by the number of water molecules in the first shell. No allowance is made for the chemical nature of the solute. This excess heat capacity has been shown to be expressed by eq 2 [ref *4*]. ΔH_{sh} is taken

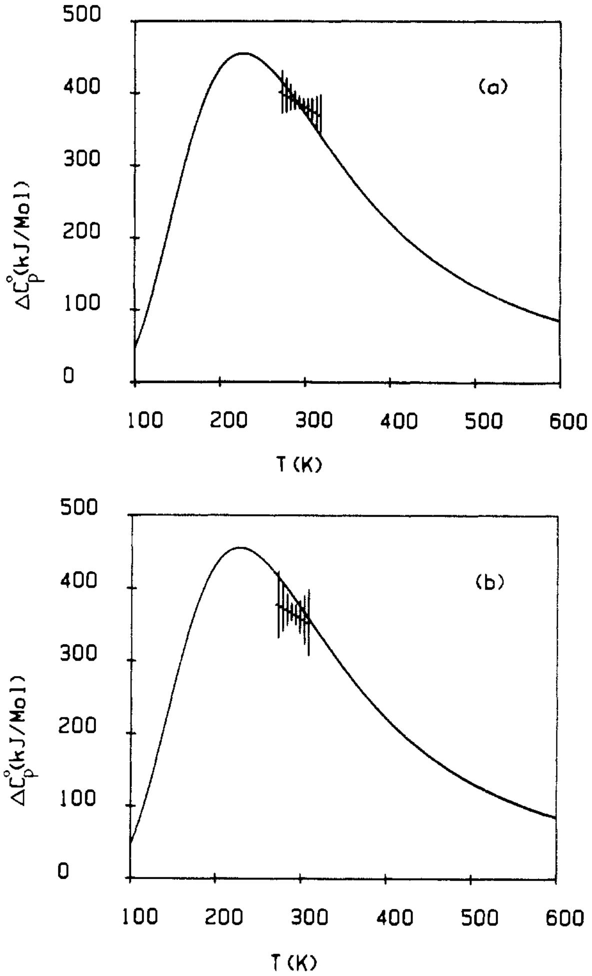

Figure 2. Heat capacity change vs. *T* for (a) *n*-butane and (b) isobutane in water. The solid lines were drawn from the predictions for an independent two-state model for solvated water with the number of solvated water molecules *N* equal to 28.4 for *n*-butane and 27.7 for isobutane. The experimental results are represented by points with vertical lines indicating twice the estimated standard error of the point as calculated by the method of Clarke and Glew (*12*).

$$\Delta C_p{}^\circ = N\frac{(\Delta H_{sh}{}^2)}{RT^2}\,\frac{e^{-(\Delta H_{sh}/R)(\tau-\tau_m)}}{[1+e^{-(\Delta H_{sh}/R)(\tau-\tau_m)}]^2} \qquad (2)$$

as 6.5 kJ/mol (i.e., on the order of a hydrogen bond), τ_m is taken as 370 K (*10*), and *N* is found to be 28.4 for *n*-butane and 27.7 for isobutane by using the surface area calculation method of Hermann (*11*). In Figure 2 our results are shown for *n*-butane (a) and isobutane (b), using the $\Delta C_p{}^\circ$ data from Tables IV and VI. As a first approximation, the model fits the experimental data quite well in both magnitude and temperature dependence, providing further support for the hypothesis that the thermodynamic parameters of hydrophobic solvation are determined primarily by the number of water molecules in the first solvation shell, and not by specific solute–solvent interactions.

Glossary

ΔH°	the standard enthalpy of solution; it is assumed that the solutions are sufficiently dilute that the standard state of an ideal 1 *m* solution, pressure of 1 atm, applies
ΔC_p°	the standard heat capacity change upon solution (the first derivative of the standard enthalpy of solution with respect to temperature)
θ	an arbitrary reference temperature used in the Taylor's series calculation of the temperature dependence of the enthalpy of solution
N	the number of water molecules in the first solvation shell
R	the gas constant
ΔH_{sh}	in eq 2, the energy difference between the two states in which water molecules in the first solvation shell can exist
τ	the reciprocal temperature ($1/T$), K^{-1}
τ_{m}	the reciprocal temperature at which the populations of the two states are equal

Registry No. *n*-Butane, 106-97-8; isobutane, 75-28-5.

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Received for review September 29, 1986. Accepted June 8, 1987. We wish to acknowledge the assistance of NSF Grant No. PCM8019930 and the University of Kerman for providing sabbatical to Dr. Hossein Naghibi.

Excess Molar Enthalpies of Seven *n*-Hexadecane + *n*-Alkylamine Binary Liquid Mixtures

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An isobaric and quasi-isothermic calorimeter has been used to determine excess molar enthalpies, H^E, as a function of concentration at atmospheric pressure and 303.15 K for seven binary liquid mixtures containing *n*-alkylamine (*n*-propyl-, *n*-butyl-, *n*-hexyl-, *n*-octyl-, *n*-decyl-, *n*-dodecyl-, and *n*-pentadecylamine) with *n*-hexadecane. The maxima of the H^E–composition curves decrease with increasing length of the aliphatic chain of amine and shift gradually toward the hexadecane-rich side.

Introduction

Measurements of thermodynamic properties on *n*-alkane + *n*-alkylamine have been reported extensively (*1*–*3*), but no suitable data are available in the literature for amines whose aliphatic radical has more than eight carbon atoms. We report here the excess molar enthalpy, H^E, at 303.15 K, for *n*-hexadecane ($C_{16}H_{34}$) + *n*-propylamine ($PrNH_2$), + *n*-butylamine ($BuNH_2$), + *n*-hexylamine ($HeNH_2$), + *n*-octylamine ($OcNH_2$), + *n*-decylamine ($DeNH_2$), and + *n*-dodecylamine ($DoNH_2$), and for $C_{16}H_{34}$ + *n*-pentadecylamine ($PeNH_2$) at 313.15 K. As far as we know, the only previous measurements on these mixtures are those of Pfestorf et al. (*1*) of H^E for $C_{16}H_{34}$ + $BuNH_2$, + $HeNH_2$, and + $OcNH_2$; their results (1838, 1508, and 1292 J mol^{-1}, respectively, at 298.15 and $x = 0.5$) are higher than ours (1731, 1433, and 1146 J mol^{-1}, respectively, at 303.15 K). Although we cannot be sure of the cause of these discrepancies, we point out that impurities in amines can be an important source of error.

Table I. Refractive Indices of Pure Amines

compound	$n^{298.15}{}_D$ this work	$n^{298.15}{}_D$ lit. (*8*)
n-propylamine	1.385 05	1.3851
n-butylamine	1.398 75	1.3987
n-hexylamine	1.416 11	1.4167
n-octylamine	1.427 03	1.4277
n-decylamine	1.434 80	1.4352
n-dodecylamine	1.433 98[a]	1.4406
n-pentadecylamine	1.439 54[a]	1.4464

[a] At 313.15 K.

Experimental Section

All the liquids used were from Fluka AG, Buchs, better than 99 mol %, except $PeNH_2$ which is better than 98 mol %. *n*-Propylamine, *n*-butylamine, and *n*-hexylamine were purified by a low-pressure distillation method described elsewhere (*4*). No further purification was made with the other liquids, although they were kept over activated molecular sieve to avoid moisture contamination. Refractive indices (Table I) and static dielectric constants of the pure liquids (*3*) agree satisfactorily with those in literature.

Excess molar enthalpies were determined by using an isobaric and quasi-isothermic calorimeter similar to that described in ref *5*. The mixing cell is an anchor-shaped glass receptacle filled under vacuum with bidistillated Hg to isolate weighed quantities of the two liquids in the limbs of the cell. A continuous pendular movement permits the two liquids to mix at constant pressure and in the complete absence of vapor phase. Electrical energy was measured to better than 0.5%, and

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