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Calorimetric Measurement of Partial Molar Excess Enthalpies at Infinite Dilution

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An asymmetric isothermal flow calorimeter was used to obtain excess enthalpies of binary liquid mixtures of nonelectrolytes in the dilute region, and these data were used to calculate partial molar excess enthalpies at infinite dilution. A variety of solutes and solvents were examined to characterize the wide range of intermolecular interactions that may occur in solution. Comparisons were made to the values of the partial molar excess enthalpy at infinite dilution obtained from the temperature dependence of limiting activity coefficient data and to heats of solution at infinite dilution.

Introduction

Accurate representation of the chemical activities in a multicomponent mixture is essential to the design of fluid-phase separation equipment. Attempts to model solution behavior are commonly centered around the molar excess Gibbs energy, g^E, as a function of mole fraction x_i and temperature T. Largely on the basis of a vast database of vapor-liquid equilibria (VLE), researchers have developed models for $g^E(x)$, such as the Wilson, NRTL, and UNIQUAC. While accurate enough to correlate VLE data successfully, current models often fail when correlating or predicting those types of solution behavioir that depend on derivatives of g^E, such as liquid-liquid equilibria (LLE) and the molar excess enthalpies (heats of mixing), h^E (*1*, *2*).

For a better understanding of solution behavior, it is advantageous to examine derivative excess properties in the limit of infinite dilution, where a single solute molecule is completely surrounded by solvent. Since solute-solute interactions are no longer present, infinite dilution excess properties reflect almost completely unlike-pair interactions and yield information about such intermolecular forces. Furthermore, by measuring derivative excess properties directly, one avoids the inherent loss of precision incurred when differentiating data. Since the integration of data may enhance precision, it is preferable to measure derivative data directly and integrate, rather than the reverse.

A number of experimental techniques have been developed in recent years for the measurement of partial molar excess properties at infinite dilution. Measurement of the activity coefficient at infinite dilution, γ_i^∞, has been widely performed through a variety of techniques—gas chromatography (*3*), headspace chromatography (*4*), differential boiling point measurement (*5-7*), and gas stripping (*8*). Furthermore, the advent of the vibrating-tube densitometer has made it relatively easy to measure the partial molar excess volume at infinite dilution, a pressure derivative of γ_i^∞ (*9*). The present work describes a calorimetric technique for measuring the partial molar excess enthalpy of component i at infinite dilution $h_i^{E\infty}$, a temperature derivative of γ_i^∞. The governing thermodynamic relationship is

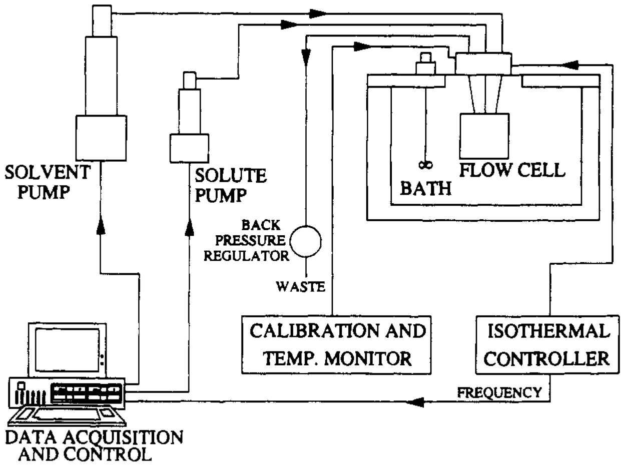

Figure 1. Schematic diagram of experimental apparatus.

$$\left[\frac{\partial \ln \gamma_i^\infty}{\partial(1/T)}\right]_{P,x} = \frac{h_i^{E\infty}}{R} \tag{1}$$

A value of $h_i^{E\infty}$ could thus be obtained by calculating the slope of a $\ln \gamma_i^\infty$ vs $1/T$ curve. Although the γ_i^∞ values themselves are often accurate to better than 5%, the differentiation procedure introduces errors of up to 1 order of magnitude when $h_i^{E\infty}$ are calculated from the γ_i^∞ temperature dependence. Thus, to obtain a precise value of the partial molar excess enthalpy at infinite dilution, a different technique is preferred.

Recent advances in calorimetry (*10-12*) have resulted in vastly improved instruments, capable of rapid and precise measurements. To obtain a value of the partial molar excess enthalpy at infinite dilution from calorimetry, one must measure heats of mixing in the dilute region and calculate the limiting slope of the excess enthalpy versus mole fraction curve as indicated by the following relationship:

$$h_1^{E\infty} = \lim_{x_1 \to 0} \left[h^E + x_2(\partial h^E/\partial x_1)\right] \tag{2}$$

Previous attempts at making these measurements have suffered largely due to imprecise values of the mole fractions in the dilute region, the stringent sensitivity requirements of measuring such small heats of mixing of dilute mixtures, and the presence of a vapor space in batch calorimeters. Modifications of existing methods have allowed sufficiently precise values of $h_i^{E\infty}$ to be measured by using an isothermal flow calorimeter with asymmetric pumps, as described below.

Apparatus and Procedure

Isothermal flow calorimetry has become very popular in recent years with the development of syringe pumps capable of delivering accurately small, pulse-free flows. Flow calorimeters have several distinct advantages over the batch calorimeters with which most data currently available have been measured

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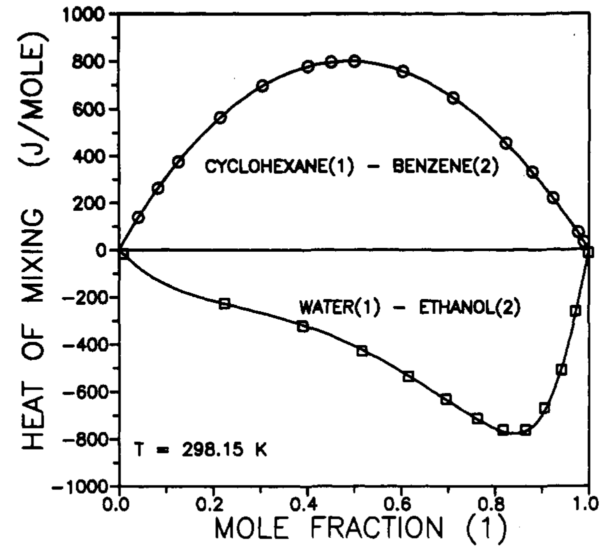

Figure 2. Calorimeter test: comparison of experimental data (open symbols) to smoothed literature data (lines) (*17*, *18*).

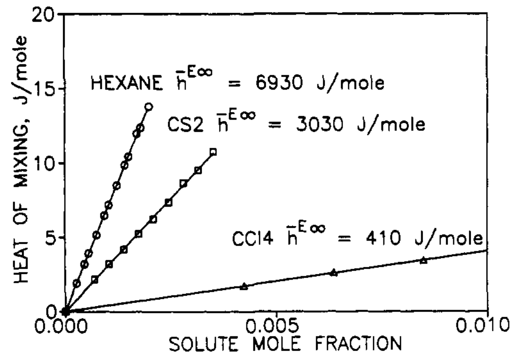

Figure 3. Sample heat of mixing data of dilute mixtures in the solvent acetone, 313.15 K.

Table I. Molar Excess Enthalpy, h^E, as a Function of Mole Fraction, x_1, for Calorimeter Test Systems (Dilute Solutions) at 298.15 K

x_1	h^E, J/mol	h^E/x_1
	For Benzene (1)–CCl_4 (2)	
	Total Flow Rate = 3 mol/h	
0.003 02	1.46	483
0.006 03	2.94	488
0.009 03	4.41	488
0.012 05	5.87	487
0.015 16	7.43	490
0.018 07	8.71	482
		$h_1^{E\infty}$ = 486 J/mol
		lit. value = 474 J/mol
	Total Flow Rate = 4 mL/h	
0.002 26	1.09	482
0.004 53	2.22	490
0.006 78	3.33	491
0.009 04	4.40	487
0.011 30	5.55	491
0.013 56	6.63	488
0.015 81	7.65	484
		$h_1^{E\infty}$ = 488 J/mol
		lit. value = 474 J/mol
	For Ethanol (1)–Water (2)	
0.000 261	−2.61	−10 000
0.000 392	−3.98	−10 170
0.000 522	−5.23	−10 020
0.000 653	−6.53	−10 000
0.000 784	−7.84	−10 000
0.000 915	−9.08	−9 930
0.001 046	−10.52	−10 060
0.001 177	−11.77	−10 000
0.001 308	−13.08	−10 000
		$h_1^{E\infty}$ = −10 020 J/mol
		lit. value = −10 210 J/mol

(*13*). The presence of a vapor space in batch calorimeters can lead to considerable error, particularly for systems having large relative volatilities. A source of error in the output baseline comes from the need to compensate for the stirrer energy input. Flow calorimeters also lend themselves readily to automation, making possible rapid data acquisition.

The isothermal flow calorimeter used for this study is the commercial unit by Hart Scientific, Model 7501-L with constant temperature bath Model 5007, capable of operation between 233 and 353 K with temperature stability of ±0.0005 K. To obtain precise values of the compositions in the dilute region, asymmetric pumps were used, as opposed to matching pumps typically used in measuring midcomposition heats of mixing. For use with the flow calorimeter, the solvent pump (ISCO, LC-5000) operates at flow rates on the order of 0.5–4 mL/min. The solute pump (ISCO, μLC-500) has a flow rate range of 2 × 10^{-5} to 0.5 mL/min in range settings of 0.002, 0.02, 0.2, and 0.6 mL/min. So with a flow rate accuracy of ±0.5%, sufficiently accurate mole fractions are obtained for the dilute region.

The isothermal flow calorimeter works by monitoring the power required by the control heater to keep the flow cell under isothermal conditions. The difference in control heater power requirement (milliwatts) between pure solvent flowing and a flowstream of solute being mixed with solvent gives the heat of mixing (after dividing by the molar flow rate). Solvent and solute flow through 1.5 ft of $^1/_{16}$-in.-o.d. tubing in the constant-temperature bath. Mixing occurs at the union of the two inlet tubes, which are electron beam welded to a small triangular mixing tee. The resulting mixture flows out the third side in $^1/_{16}$-in.-o.d. tubing, which winds down a cylindrical heat sink block. Control sensors, located close to the exit point of the flow tube, sense the temperature. The control heater regulates the energy flow through the flow cell heat sink such that isothermal conditions are maintained. The flow tubing, heat sink block, and related electronics (control heater, control sensor, Peltier cooler, temperature sensor, calibration heater) are located in a stainless steel canister that is immersed in the constant-temperature bath. A diagram of the flow calorimeter apparatus is given in Figure 1.

Data acquisition and control is provided by an IBM PC. The LC-5000 syringe pump is automated through an installed RS232 interface. The μLC-500 pump is interfaced with the computer through a Metrabyte DAS-16 analog and digital interface board. The frequency of electrical pulses supplied to the control heater (counts per second) is fed to the computer through a LabTender Interface Card, as supplied by Hart Scientific.

For operation, the bath temperature and the calorimeter flow cell temperature are set and allowed to equilibrate overnight. Before the run can begin, some preliminary tests are necessary. First, it must be established whether the heating is endothermic or exothermic. Also, for measuring $h_i^{E\infty}$, it is advantageous to make h^E measurements as dilute as possible. However, due to sensitivity limits of the heat measurement, an excessive amount of noise may be present in the control heater base line, preventing meaningful results from being obtained. The magnitude of the fluctuations differ from system to system, depending largely on how readily the components mix. For example, the noise in the baseline for the hexane–cyclohexane system is well within the manufacturer's specification of ±50 μW. Thus, the optimum heating sensitivity is that which is most

Table II. Partial Molar Excess Enthalpy at Infinite Dilution, $h_1^{E\infty}$, at Temperature T Obtained by Direct Calorimetry (calorim) or from the Temperature Dependence of the Activity Coefficient at Infinite Dilution (γ_1^∞ vs T) in the Given T Range

			$h_1^{E\infty}$, J/mol		
solute (1)	solvent (2)	T, K	calorim	γ_1^∞ vs T	T range, K
2-butanone	acetone	313.15	184 ± 3	0	298–329
CS_2	acetone	313.15	3310 ± 70	5400	301–329
CCl_4	acetone	313.15	446 ± 7	740	301–329
chloroform	acetone	313.15	−3530 ± 90	−2000	301–328
1,4-dioxane	acetone	313.15	415 ± 11	0	298–329
ethanol	acetone	313.15	4750 ± 60	6400	298–329
heptane	acetone	313.15	8570 ± 160		
hexane	acetone	313.15	7630 ± 80	7800	301–328
nitromethane	acetone	313.15	−747 ± 22		
nonane	acetone	313.15	10700 ± 100		
octane	acetone	313.15	9740 ± 70	12600	298–329
toluene	acetone	313.15	1080 ± 10	4400	298–329
acetone	CS_2	313.15	7940 ± 90	5800	298–319
butanone	CS_2	313.15	6570 ± 110	4000	298–319
1,4-dioxane	CS_2	313.15	5750 ± 90	4700	298–319
ethanol	CS_2	313.15	21500 ± 500	17900	303–319
nitromethane	CS_2	313.15	13500 ± 100	11700	298–319
toluene	CS_2	313.15	1900 ± 40	4800	298–319
acetone	CCl_4	328.15	3650 ± 100	5400	329–344
1-propanol	CCl_4	328.15	17200 ± 100	18200	315–344
1-butanol	cyclohexane	313.15	23500 ± 200	21500	313–353
ethanol	cyclohexane	313.15	23200 ± 200	21500	313–353
hexane	cyclohexane	298.15	1170 ± 10	1200	324–353
1-pentanol	cyclohexane	313.15	23800 ± 300	22600	313–353
2-propanol	cyclohexane	313.15	21300 ± 300	18100	313–353
chloroform	ethyl acetate	328.15	−3540 ± 110	−4400	311–350
chloroform	hexane	323.15	2370 ± 110	2300	302–341
2-butanone	methanol	323.15	2800 ± 90	2900	309–337
cyclohexane	methanol	323.15	5540 ± 40	7000	307–337
1,4-dioxane	methanol	323.15	4590 ± 120	3500	309–337
ethanol	methanol	323.15	−19 ± 3		
nitromethane	methanol	323.15	4650 ± 60	8400	309–337
toluene	methanol	323.15	2860 ± 80	2600	309–337
cyclohexane	2-propanol	333.15	4280 ± 90	2800	313–355
heptane	2-propanol	333.15	5250 ± 100	4400	324–355
n-hexane	2-propanol	333.15	4540 ± 40	3400	324–355
methylcyclohexane	2-propanol	333.15	4250 ± 60	4800	324–355
toluene	2-propanol	333.15	6010 ± 20	6700	313–355

sensitive but still gives base-line noise less than about ±1000 Hz (±1% of scale). The solute flow rate that gives the maximum heat change on the chosen heating range is also determined during this prerun testing. This prerun planning can also be facilitated by examining other literature data.

At the start of the run, pure solvent is flowed through the cell, and the constant cooling input is adjusted to bring the control heater input to between 10–15 kHz for endothermic mixing and between 85–90 kHz for exothermic mixing. Next, the calorimeter flow cell temperature setpoint is fine-tuned so that the incoming flowstreams are the same temperature as the calorimeter, to eliminate sensible heating effects. This is accomplished by simply adjusting the calorimeter temperature setpoint until the control heater base line is the same when solvent is flowing through the flow cell as when there is zero flow. The chemical run is begun by starting the flow of solute. The response was much faster when the maximum solute concentration (determined earlier) was started first, with subsequent measurements made for the more dilute mole fractions. The total volumetric flow rate was kept constant for all measurements. At each composition, the frequency of electrical pulses supplied to the control heater was averaged over a 10–15-min time span. Typically, h^E was measured at 6–10 dilute concentrations to obtain $h_i^{E\infty}$. The volumetric flow rate of the fluids supplied by the pumps at 298 K was converted to molar flow rate by using the molar volume given by the Rackett equation (*14*) or from Riddick et al. (*15*).

Calibration of the pump flow rate was performed by flowing water through the system, collecting it in a volumetric flask while timing, and then weighing. Replicate trials gave reproducible results within ±0.5%. Two alternatives exist for the calibration of the control heater, to convert counts per second to milliwatts (or volts to milliwatts in the case of a strip chart recorder). The flow cell is equipped with a calibration heater that simulates an exothermic reaction by supplying a known amount of heat (milliwatts) through the flow tubing. The calibration constant obtained in this manner (microjoules per count or milliwatts per volt) gave the results that, when compared to well-established literature data, were consistently 3–4% too small for both endothermic and exothermic mixing. So, for this study, chemical calibration was performed on the basis of the well-established hexane–cyclohexane system (*16*), for which the heat of mixing is relatively small—a good basis for the small h^E values of dilute solutions to be measured in this study. With use of the calibration constant obtained in this manner, several test systems were studied for comparison to literature data (*17*–*18*). These are shown in Figure 2 and Table I.

As seen in Table I and in subsequent trials, there was no dependence of the result on the total flow rate, with 4 mL/min being the manufacturer's recommended limit. Higher flow rates result in the mixture leaving the isothermal flow cell without being completely equilibrated at the temperature of the cylinder (*19*). Also examined was the frictional energy that comes about when the two components are mixed at the mixing tee. There was no observed change in the control heater baseline between flowing water through the system with the solvent pump alone and pumping water simultaneously through the cell from the solute pump at various flow rates.

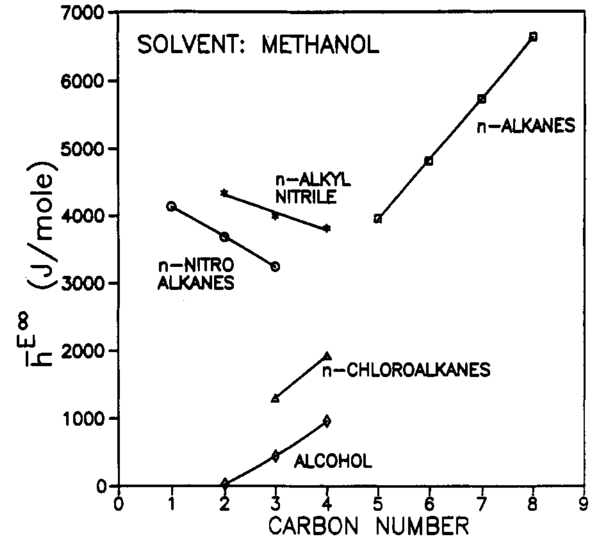

Figure 4. $h_i^{E\infty}$ data for homologous series of solutes in the solvent methanol, 298.15 K.

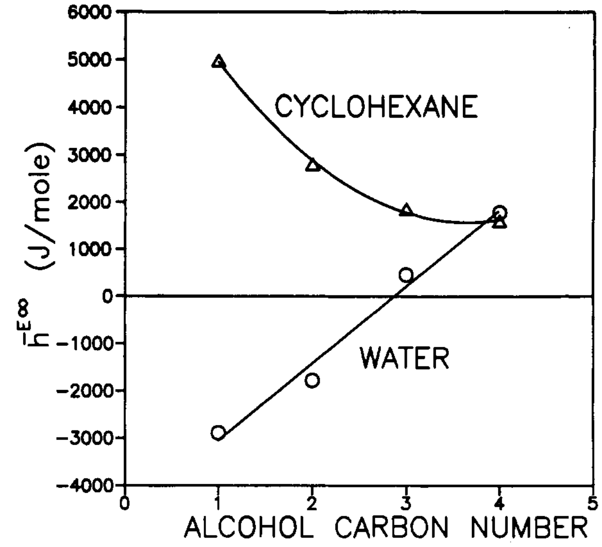

Figure 5. $h_i^{E\infty}$ data for water and cyclohexane as solute in a homologous series of alcohols as solvent.

Materials

The solvents used in this experiment should have a purity of 99.9+%. The solute purity is less critical, but it should be at least 99%. Purifications were performed as deemed necessary. Refractive index values, n_D, are at 293 K, measured with an Abbe Model Refractometer (stated accurately is ±0.0001).

The following chemicals were used: acetone, Mallinckrodt Nanograde, used as purchased; benzene, Aldrich HPLC Grade, 99.9%, used as purchased; 1-butanol, Mallinckrodt Nanograde, $n_D = 1.3995$, used as purchased; butanone, Baker Analyzed Reagent, 99.6%, used as purchased; butyronitrile, Aldrich, fractionally distilled with middle 60% collected, $n_D = 1.3839$; carbon disulfide, Mallinckrodt Reagent Grade, fractionally distilled with middle 60% collected; carbon tetrachloride, Baker Analyzed Reagent, 99.9+%, $n_D = 1.4595$, used as purchased; 1-chlorobutane, Aldrich, HPLC grade, 99.9%, $n_D = 1.4026$; chloroform, Baker Analyzed Reagent, ethanol as stabilizer, or Aldrich, 99.9%, $n_D = 1.4461$, amylenes as stabilizer, used as purchased; 1-chloropropane, Aldrich, 99%, $n_D = 1.3880$, used as purchased; cyclohexane, Mallinckrodt Nanograde, $n_D = 1.4268$, used as purchased; decane, Aldrich, 99+%, used as purchased; dichloromethane, Mallinckrodt Nanograde, used as purchased; diethyl ether, Mallinckrodt Nanograde, use as purchased within 2 days of opening container; 1,4-dioxane, Baker Analyzed Reagent, 99.9+%, used as purchased; ethanol, Midwest Grain Products, $n_D = 1.3625$, dried over 3A molecular sieves; ethyl acetate, Baker Analyzed Reagent, 99.9+%, used as purchased; heptane, Aldrich, HPLC Grade, 99+%, $n_D = 1.3879$, used as purchased; hexadecane, Aldrich, 99+%, used as purchased; hexane, Mallinckrodt ChromAR Grade, $n_D = 1.3753$, used as purchased; methanol, Mallinckrodt Nanograde, $n_D = 1.3284$, dried over 3A molecular sieves; 2-methylpentane, Aldrich, 99+%, $n_D = 1.3715$, used as purchased; methylcyclohexane, Aldrich, Anhydrous, 99+%, used as purchased; nitroethane, Aldrich, 99.5%, $n_D = 1.3920$, used as purchased; nitromethane, Aldrich, fractionally distilled with middle 60% collected; nitropropane, Aldrich, fractionally distilled with middle 60% collected; nonane, Aldrich, 99+%, $n_D = 1.4059$, used as purchased; octane, Aldrich, anhydrous, 99+%, $n_D = 1.3977$, used as purchased; pentane, Mallinckrodt Nanograde, used as purchased; 1-pentanol, Aldrich, 99+%, used as purchased; 1-propanol, Baker Analyzed Reagent, 99.9+%, $n_D = 1.3854$, used as purchased; 2-propanol, Baker Analyzed Reagent, fractionally distilled with middle 60% collected; propionitrile, Aldrich, 99%, $n_D = 1.3361$, used as purchased; tetradecane, Aldrich, 99%, used as purchased; tetrahydrofuran, Mallinckrodt ChromAR Grade, used as purchased; toluene, Baker Analyzed Reagent, 99.9+%, used as purchased; water, Mallinckrodt ChromAR Grade, used as purchased.

Results

Sample heat of mixing data obtained in the dilute region by using this technique are given in Figure 3. To calculate $h_i^{E\infty}$, the h^E vs x values were fit to the expression

$$h^E/x_1 = A + Bx_1 \qquad (3)$$

$$h_1^{E\infty} = A$$

In most cases, h^E/x_1 was constant over the composition range studied, within experimental error. The value of $h_i^{E\infty}$ reported is the average of all h^E/x_1 values. The estimate of the precision reported in the data tables is the maximum deviation from the average of all h^E/x_1 values at the various compositions. The complete set of x_1, h^E, and h^E/x_1 values measured are given in the supplementary material.

The first data set, Table II, is for those systems for which γ_i^∞ vs temperature measurements were made previously (*7*). This provides a complete set of both γ_i^∞ and $h_i^{E\infty}$ values, as well as demonstrating the error associated with the attempt to differentiate γ_i^∞ data to obtain $h_i^{E\infty}$. The temperature chosen for the calorimetric measurement of $h_i^{E\infty}$ was usually the midpoint of the temperature range over which γ_i^∞ was measured. The values of $h_i^{E\infty}$ from γ_i^∞ vs T measurements, as compared to the more precise calorimetric values, are seen to be only a semiquantitative estimate, particularly for small values of $h_i^{E\infty}$, where the change in γ_i^∞ with temperature is small. The greater the change in γ_i^∞ with temperature (larger $h_i^{E\infty}$), the better the agreement between the two techniques. For $h_i^{E\infty}$ values above 10 000 J/mol, the differences are less than 20%. Thus, Table II demonstrates the focus of this work—development of a technique to measure directly $h_i^{E\infty}$, more accurately and faster than by the differentiation of γ_i^∞ vs T data.

Data were taken for a set of homologous series of solutes (alkenes, alcohols, nitroalkanes, alkanenitriles, and chlorinated compounds) in seven solvents (cyclohexane, methanol, diethyl ether, dichloromethane, acetonitrile, water, and nitromethane) to characterize the wide range of intermolecular interactions that may occur in solution. The results are given in Table III.

Table III. Partial Molar Excess Enthalpy at Infinite Dilution, $h_1^{E\infty}$, at 298.15 K Obtained by Direct Calorimetric Measurement of the Molar Heat of Mixing, h^E, in the Given Mole Fraction x_1 Range, Equation 3

solute (1)	$h_1^{E\infty}$, J/mol	x_1 range	solute (1)	$h_1^{E\infty}$, J/mol	x_1 range
(a) Solvent: Cyclohexane					
pentane	1030 ± 40	0.0623–0.00775	acetonitrile	15000 ± 300	0.00432–0.000866
hexane	1170 ± 10	0.0138–0.00345	propionitrile	12600 ± 100	0.00572–0.00127
heptane	1600 ± 20	0.0108–0.00307	butyronitrile	10200 ± 200	0.00719–0.00205
octane	1750 ± 30	0.00909–0.00209	1-chloropropane	3080 ± 20	0.0228–0.00761
decane	2160 ± 10	0.00754–0.00115	1-chlorobutane	2890 ± 50	0.0258–0.00860
dodecane	2670 ± 20	0.00637–0.000791	dichloromethane	5350 ± 100	0.0153–0.00558
tetradecane	3160 ± 30	0.00525–0.000696	chloroform	2870 ± 80	0.0251–0.00840
hexadecane	3720 ± 60	0.00419–0.000463	carbon tetrachloride	622 ± 24	0.110–0.0186
2-methylpentane	980 ± 30	0.0621–0.00681	acetone	10800 ± 300	0.00609–0.00122
methanol	20900 ± 200	0.00346–0.00116	2-butanone	8640 ± 100	0.00802–0.00100
ethanol	23300 ± 500^a	0.00313–0.000782	benzene	3190 ± 30	0.0226–0.00505
1-propanol	23600 ± 500^a	0.00313–0.000940	toluene	2940 ± 30	0.0254–0.00635
1-butanol	23500 ± 500^a	0.00391–0.000652	diethyl ether	2300 ± 50	0.0300–0.00428
1-pentanol	24100 ± 500^a	0.00388–0.00111	tetrahydrofuran	3200 ± 60	0.0221–0.00555
nitromethane	16500 ± 400	0.00419–0.000839			
nitroethane	12700 ± 300	0.00597–0.00126			
1-nitropropane	10900 ± 200	0.00659–0.00304			
(b) Solvent: Methanol					
pentane	3960 ± 20	0.00636–0.000699	acetonitrile	4340 ± 50	0.00578–0.000936
hexane	4820 ± 40	0.00535–0.00125	propionitrile	3990 ± 30	0.00692–0.00184
heptane	5730 ± 60	0.00476–0.000553	butyronitrile	3810 ± 20	0.00748–0.00927
octane	6630 ± 50	0.00406–0.000502	1-chloropropane	1300 ± 30	0.0197–0.00553
2-methylpentane	4550 ± 30	0.00590–0.00123	1-chlorobutane	1930 ± 30	0.0143–0.00468
cyclohexane	4980 ± 70	0.00530–0.00150	dichloromethane	−1800 ± 110	0.00328–0.00101
ethanol	26.8 ± 1.5	0.107–0.0113	chloroform	−5000 ± 50	0.00559–0.00152
1-propanol	445 ± 4	0.0131–0.00340	carbon tetrachloride	−636 ± 20	0.00935–0.00168
1-butanol	962 ± 11	0.00621–0.00176	water	−2890 ± 30	0.00985–0.00270
nitromethane	4140 ± 50	0.00682–0.00227			
nitroethane	3680 ± 50	0.00741–0.00284			
1-nitropropane	3240 ± 40	0.00925–0.00275			
(c) Solvent: Diethyl Ether					
pentane	1340 ± 30	0.0113–0.00377	nitromethane	1770 ± 40	0.0400–0.0122
hexane	1500 ± 20	0.0101–0.00336	nitroethane	1420 ± 50	0.0542–0.00611
heptane	1720 ± 30	0.00898–0.00299	1-nitropropane	830 ± 40^a	0.1163–0.00986
octane	1940 ± 20	0.00816–0.00271	acetonitrile	2140 ± 50	0.0352–0.00839
2-methylpentane	1460 ± 30	0.0108–0.00165	propionitrile	1780 ± 30	0.0428–0.0123
cyclohexane	1700 ± 30	0.0101–0.00203	butyronitrile	1170 ± 60	0.0594–0.00998
methanol	3820 ± 60	0.0178–0.00225	1-chloropropane	−599 ± 4	0.0271–0.00247
ethanol	5180 ± 110	0.0136–0.00304	1-chlorobutane	−550 ± 5	0.0314–0.004-18
1-propanol	5070 ± 50	0.0146–0.00183	chloroform	−8130 ± 140	0.00953–0.00273
1-butanol	5260 ± 110	0.0133–0.00380	carbon tetrachloride	−1950 ± 20	0.0406–0.00905
(d) Solvent: Dichloromethane					
pentane	6360 ± 50	0.00650–0.000925	nitromethane	840 ± 40^a	0.0545–0.00500
hexane	7080 ± 40	0.00579–0.000823	nitroethane	−858 ± 14	0.0103–0.00188
heptane	8040 ± 50	0.00515–0.000732	1-nitropropane	−1420 ± 40	0.00667–0.00151
octane	8810 ± 50	0.00468–0.000665	acetonitrile	−1820 ± 30	0.00516–0.000516
2-methylpentane	6980 ± 30	0.00612–0.000811	propionitrile	−2930 ± 40	0.00323–0.000760
cyclohexane	6070 ± 30	0.00699–0.000994	butyronitrile	−3160 ± 90	0.00276–0.000613
methanol	11600 ± 200	0.00379–0.000689	1-chloropropane	315 ± 5	0.0275–0.00303
ethanol	12700 200	0.00326–0.000467	1-chlorobutane	749 ± 11	0.0116–0.00128
1-propanol	13400 ± 100	0.00336–0.000374	chloroform	74.9 ± 1	0.0611–0.0202
1-butanol	14400 ± 100	0.00292–0.000291	carbon tetrachloride	2330 ± 50	0.00417–0.00111
(e) Solvent: Acetonitrile					
pentane	8950 ± 120	0.00356–0.000373	propionitrile	210 ± 5	0.0167–0.00368
hexane	10340 ± 150	0.00317–0.000332	butyronitrile	868 ± 14	0.00446–0.000742
heptane	12080 ± 170	0.00282–0.000295	1-chloropropane	2480 ± 5	0.00294–0.000978
octane	13420 ± 150	0.00256–0.000268	1-chlorobutane	3510 ± 70	0.00228–0.000828
2-methylpentane	9940 ± 200	0.00329–0.000327	dichloromethane	−767 ± 12	0.0203–0.00539
cyclohexane	9800 ± 110	0.00342–0.000803	chloroform	−1470 ± 40	0.0109–0.00270
methanol	5660 ± 100	0.00611–0.00111	carbon tetrachloride	2980 ± 70	0.00472–0.00134
ethanol	7880 ± 100	0.00452–0.000753	water	7440 ± 170	0.00480–0.00120
1-propanol	8840 ± 170	0.00393–0.000603			
1-butanol	10290 ± 170	0.00330–0.000470			
nitromethane	−50.1 ± 1.1	0.0728–0.00807			
nitroethane	−101 ± 2	0.0337–0.00607			
1-nitropropane	489 ± 10	0.00785–0.00196			

Table III (Continued)

solute (1)	$h_1^{E\infty}$, J/mol	x_1 range	solute (1)	$h_1^{E\infty}$, J/mol	x_1 range
(f) Solvent: Water					
methanol	−7 000 ± 70	0.001 84–0.000 289	acetonitrile	−1 490 ± 20	0.000 868–0.000 144
ethanol	−10 020 ± 150	0.001 31–0.000 261	propionitrile	−3 290 ± 110	0.000 351–0.000 106
1-propanol	−9 900 ± 160	0.001 31–0.000 314	butyronitrile	−2 390 ± 40	0.000 515–0.000 172
1-butanol	−8 740 ± 110	0.001 47–0.000 163			
nitromethane	3 520 ± 40	0.003 52–0.000 840			
nitroethane	909 ± 36	0.001 26–0.000 210			
1-nitropropane	490 ± 8	0.002 56–0.000 849			
(g) Solvent: Nitromethane					
pentane	12 800 ± 100	0.002 70–0.000 385	acetonitrile	−34.0 ± 0.4	0.103–0.025 8
hexane	14 500 ± 100	0.002 40–0.000 341	propionitrile	801 ± 9	0.004 91–0.001 27
heptane	14 500 ± 100	0.002 14–0.000 305	butyronitrile	1 900 ± 20	0.001 92–0.000 511
octane	14 300 ± 300	0.002 50–0.000 277	1-chloropropane	5 010 ± 40	0.006 59–0.001 01
2-methylpentane	13 900 ± 200	0.002 63–0.000 338	1-chlorobutane	6 620 ± 80	0.005 15–0.000 641
cyclohexane	13 600 ± 300	0.002 70–0.000 414	dichloromethane	1 140 ± 40	0.007 30–0.001 04
methanol	9 290 ± 80	0.004 02–0.000 575	chloroform	1 100 ± 20	0.007 27–0.001 12
ethanol	11 970 ± 70	0.003 11–0.000 389	carbon tetrachloride	5 690 ± 90	0.006 51–0.000 926
1-propanol	13 680 ± 110	0.002 65–0.000 311	water	14 000 ± 300	0.025 6–0.003 72
1-butanol	16 000 ± 200	0.002 31–0.000 243			
nitroethane	447 ± 5	0.008 15–0.001 09			
1-nitropropane	1 470 ± 20	0.002 53–0.000 757			

[a] h^E/x_1 composition-dependent.

Table IV. Partial Molar Excess Enthalpy at Infinite Dilution, $h_1^{E\infty}$, at 298.15 K Obtained by Direct Calorimetric Measurement of the Molar Heat of Mixing, h^E, in the Given Mole Fraction x_1 Range, Equation 3

	solute (1)			
	water		cyclohexane	
solvent (2)	$h_1^{E\infty}$, J/mol	x_1 range	$h_1^{E\infty}$, J/mol	x_1 range
methanol	−2890 ± 30	0.009 85–0.002 70	4980 ± 70	0.005 30–0.001 50
ethanol	−1780 ± 70	0.009 26–0.001 33	2810 ± 20	0.013 5–0.001 78
1-propanol	460 ± 22	0.037 7–0.004 97	1860 ± 30	0.028 1–0.003 05
1-butanol	1790 ± 30	0.029 1–0.004 25	1610 ± 20	0.039 3–0.003 91

Figure 4 shows the linear relationship that is often observed between $h_i^{E\infty}$ and the carbon number for a homologous series of solutes in a solvent (methanol in this case). There seems to be no general rule governing the direction of change in $h_i^{E\infty}$ with carbon number within each homologous series. However, when the solutes are of the same class as the solvent (such as alcohols in methanol), $h_i^{E\infty}$ appears to increase with carbon number. Also, $h_i^{E\infty}$ for 2-methylpentane falls between the value for *n*-pentane and *n*-hexane (except in cyclohexane).

The opposite approach was also undertaken whereby $h_i^{E\infty}$ of a solute was measured in a homologous series of alcohols as solvent. The results are presented in Table IV and Figure 5 for the solutes water and cyclohexane.

Table V is a comparison of data from this study with those from the literature. The first comparison is with values of $h_i^{E\infty}$ obtained from dilute heat of mixing data, as compiled by Matuszak (*20*), who found only 17 systems for which sufficiently dilute h^E values were reported. The paucity of this type of data is one reason why this study was undertaken.

A second comparison is with an analogous technique where the heat change is measured upon additions (10–50 μL) of solute to 75–200 mL of solvent in a batch solution calorimeter and reported as the molar heat of solution at infinite dilution, ΔH_s^∞. With a few exceptions, agreement is within ±10%, with no systematic differences, indicating the compatibility of the data taken by the two techniques. For some binary pairs, replicate values are reported in the literature. For Table V, the value reported is that most recently published. All values for benzene in carbon tetrachloride and acetone in cyclohexane are given to indicate the type of discrepancies that may be seen between data of different researchers using the same technique. The precision is typically reported as ±2% for $\Delta H_s^\infty >$ 4000 J/mol and ±100 J/mol for $\Delta H_s^\infty <$ 4000 J/mol.

Discussion and Summary

An asymmetric isothermal flow calorimeter was developed specifically for the accurate measurement of partial molar excess enthalpies at infinite dilution of binary solutions of nonelectrolytes. The instrument was successfully tested against literature data and found to be accurate and, with computer control and data acquisition, quite rapid. Approximately 200 new data are reported.

The data reported here have tremendous potential for understanding the behavior of solutions. Evaluation of solution thermodynamics depends on two factors: the forces between molecules, especially unlike molecules, and the adding-up procedure or functional dependence. Values of $h_i^{E\infty}$ constitute a direct measure of the unlike-pair interactions, independent of any form of $g^E(x)$.

We hope that an understanding of the need to separate the study of intermolecular forces from $g^E(x)$ will lead to improvements in the composition and temperature dependence of excess Gibbs energy expressions. We and others (*1*, *2*, *37*) have shown that currently available $g^E(x)$ expressions fail when attempting to cross-predict various types of solution behavior (VLE, LLE, h^E, γ^∞). No single data set can be used to determine generally valid adjustable parameters for a $g^E(x)$ expression that will reliably predict other solution behavior.

The temperature dependence of the $g^E(x)$ equations has been under investigation to improve the correlation and prediction of h^E and of VLE over a broader temperature range (*38*, *39*). The $h_i^{E\infty}$ values, indicating a maximum nonideality for the solute, could provide greater insight than midcomposition h^E data. An analogous application of the $h_i^{E\infty}$ data is as a basis for improving the temperature dependence of predictive techniques for limiting activity coefficients such as MOSCED (*40*).

Table V. Partial Molar Excess Enthalpy at Infinite Dilution, $h_1^{E\infty}$, at 298.15 K Comparison of Data from This Study with Literature Values Obtained from Direct Calorimetric Heat of Mixing or Heat of Solution Measurements in Dilute Solutions

		$h_1^{E\infty}$, J/mol		
solute (1)	solvent (2)	this study	lit.	% difference
ethanol	cyclohexane	23 300	24 060 (*21*)^a	−3.2
benzene	CCl_4	487	474 (*17*)^a	+2.7
ethanol	water	−10 020	−10 210 (*18*)^a	−1.9
cyclohexane	acetonitrile	9 800	9 020 (*22*)	+8.3
hexane	acetonitrile	10 340	9 920	+4.1
benzene	CCl_4	487	540 (*23*)	−10.3
benzene	CCl_4	487	590 (*24*)	−19.1
benzene	CCl_4	487	460 (*25*)	+5.7
1-butanol	cyclohexane	23 500	24 900 (*26*)	−5.8
1-chlorobutane	cyclohexane	2 890	3 000 (*27*)	−3.7
1-pentanol	cyclohexane	24 100	24 100 (*26*)	0.0
1-propanol	cyclohexane	23 600	24 500 (*27*)	−3.7
2-butanone	cyclohexane	8 640	8 110 (*27*)	+6.3
acetone	cyclohexane	10 800	10 030 (*27*)	+7.4
acetone	cyclohexane	10 800	9 740 (*28*)	+10.3
acetone	cyclohexane	10 800	11 300 (*29*)	−4.5
acetonitrile	cyclohexane	15 000	15 000 (*27*)	0.0
benzene	cyclohexane	3 190	3 980 (*27*)	−22.0
CCl_4	cyclohexane	622	620 (*27*)	+0.3
chloroform	cyclohexane	2 870	2 500 (*30*)	+13.8
decane	cyclohexane	2 160	2 300 (*31*)	−6.3
dodecane	cyclohexane	2 670	2 900 (*31*)	−8.3
ethanol	cyclohexane	23 300	23 900 (*27*)	−2.5
heptane	cyclohexane	1 600	1 600 (*31*)	0.0
hexadecane	cyclohexane	3 720	4 100 (*31*)	−9.7
hexane	cyclohexane	1 170	1 100 (*31*)	+6.2
methanol	cyclohexane	20 900	24 300 (*27*)	−15.0
octane	cyclohexane	1 750	1 800 (*32*)	−2.8
pentane	cyclohexane	1 030	1 100 (*31*)	−6.5
tetradecane	cyclohexane	3 160	3 100 (*31*)	+1.9
tetrahydrofuran	cyclohexane	3 220	3 400 (*27*)	−5.4
toluene	cyclohexane	2 940	3 200 (*33*)	−8.5
cyclohexane	dichloromethane	6 070	5 860 (*22*)	+3.5
chloroform	diethyl ether	−8 130	−9 100 (*30*)	−11.3
cyclohexane	diethyl ether	1 700	1 590 (*22*)	+6.7
ethanol	diethyl ether	5 180	5 400 (*30*)	−4.2
hexane	diethyl ether	1 500	1 670 (*22*)	−10.7
methanol	diethyl ether	3 820	2 300 (*30*)	+49.6
1-butanol	methanol	962	880 (*26*)	+8.9
CCl_4	methanol	−636	−550 (*34*)	+14.5
chloroform	methanol	−5 000	−4 700 (*30*)	+6.2
cyclohexane	methanol	4 980	4 940 (*31*)	+0.8
heptane	methanol	5 730	5 810 (*31*)	−1.4
hexane	methanol	4 820	5 020 (*22*)	−4.1
octane	methanol	6 630	6 610 (*31*)	+0.3
pentane	methanol	3 960	4 230 (*31*)	−6.6
chloroform	nitromethane	1 100	400 (*30*)	+93.3
cyclohexane	nitromethane	13 600	12 800 (*22*)	+6.1
hexane	nitromethane	14 500	13 810 (*22*)	+4.9
1-butanol	water	−8 740	−9 315 (*35*)	−6.4
1-propanol	water	−9 900	−9 810 (*36*)	+0.9
acetonitrile	water	−1 490	−1 560 (*36*)	−4.6
ethanol	water	−10 020	−9 750 (*36*)	+2.7
methanol	water	−7 000	−7 050 (*36*)	−0.7
nitromethane	water	3520	3 390 (*36*)	+3.8

^{a} $h_1^{E\infty}$ from dilute h^E vs x_1 measurements (*24*).

The temperature dependence of the parameters (polarity, acidity, basicity) in MOSCED is given as simple power law expressions and was based solely on a quite limited database of γ_i^∞ versus temperature data. The more sensitive $h_i^{E\infty}$ data provide a much better foundation on which to model the temperature dependence of γ_i^∞. This will allow more confident predictions of γ_i^∞ over a broader temperature range, enhancing the capability of the technique of using γ_i^∞ to model VLE behavior (*41*).

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Supplementary Material Available: Listings of all heat of mixing data measured for this study for the calculation of $h_i^{E\infty}$, with the value of h^E/x_1 also reported at each composition (72 pages). Ordering information is given on any current masthead page.