Flow microcalorimetry on dilute polymer solutions

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A flow microcalorimeter designed to measure the heat of mixing of dilute polymer solutions is described. The instrument is sensitive to steady state heating rates of ~10 μJ/sec. Measurements of heats of mixing of solutions of differing concentrations of n-hexane and cyclohexane are reported and are compared with recommended data of McGlashan and Stoeckli. Values of:

$$\kappa_1 = \lim_{v_2 \to 0} (\bar{H}_1 - \bar{H}_1^0)/RTv_2^2$$

are obtained for four polymer–solvent systems: polyisobutylene–benzene, 0.22; polystyrene (PS)–cyclohexane, 0.33; PS–n-butyl acetate, –0.06 all at 25°C; and PS–toluene, –0.05 at 40°C. Various theoretical calculations of second virial coefficients A_2 made with use of the calorimetric data are compared with previously measured A_2 for the first two mixtures.

INTRODUCTION

Dilute solution characteristics of high polymers are dependent upon values assumed by the binary segmental excluded volume integral. The evaluation of the integral in the approximation first conceived by Flory yields theoretical expressions which depend upon the microscopic enthalpy (κ_1) and entropy (ψ_1) of mixing polymer segments with solvent, defined respectively by

$$\kappa_1 = \lim_{v_2 \to 0} (\bar{H}_1 - \bar{H}_1^0)/RTv_2^2$$

and

$$\psi_1 = \lim_{v_2 \to 0} (\bar{S}_1 - \bar{S}_1^0)/Rv_2^2$$

where v_2 is the volume fraction of polymer, and other symbols have their usual significance. From the temperature coefficient of the second virial coefficient at the theta point for example, it is possible to determine an experimental value for ψ_1, thereby to provide one of the essential parameters for analysis of solution properties.

However, for solutions far from the theta temperature there is no such direct method for determination of the microscopic thermodynamic parameters. Observed solution properties for such mixtures are markedly dependent upon the configuration of the polymer chain. Analysis of such properties to deduce mixing parameters can only be accomplished by resorting to one or another theory for the configuration dependence, whereupon a circular chain of evidence is constructed so as to practically eliminate any hope of making distinctions between theories or of uncovering the source of inaccuracies in any one.

Clearly, the more pertinent information that can be gathered on dilute solutions the greater are the chances of clarifying the underlying influence of chain configuration and its subtle interplay with mixing thermodynamics. Calorimetric measurement of heats of dilution provides such additional information. While calorimetry does not supply data that could not be obtained in other ways (specifically, from the temperature coefficient of the second virial coefficient), it has accuracy to recommend it.

With these considerations in mind, we have constructed and tested a flow microcalorimeter designed for direct differential measurement of the partial molar enthalpy of the solvent. Previous calorimetry[1–6] on polymer solutions has been carried out using the integral method, in order to measure the heats of mixing small quantities of pure polymer with large volumes of pure solvent. The interesting κ_1 parameter is then obtained from the concentration dependence of the integral heats. The advantage to be gained from the differential method to be described is that the measured heat effect is virtually proportional to κ_1. Hence, instead of measuring large numbers, and taking their differences, one may make direct measurements of the small quantity.

The systems investigated are (1) polyisobutylene–benzene; (2) polystyrene (PS)–cyclohexane; (3) PS–toluene; and (4) PS–n-butyl acetate. Results obtained by the differential flow method are compared with other data in the literature where possible. In addition to the measurements, we report comparisons between theoretical calculations and previously measured second virial coefficients.

METHOD

The flow calorimeter to be described has been designed to measure the steady state rate of heat production from the mixing of flowing solutions differing in concentration. Two different methods of analysis are used to reduce the data; those methods are now to be described.

In the first case, that of small molecule mixtures where the purpose is to compare measured with published heats, the data are conveniently analysed as follows. Let the molar enthalpy of mixing $\Delta\bar{H}_M$ of pure components be given by:

$$\Delta\bar{H}_M = X_1X_2 \sum_{n=0}^{\infty} A_n(X_2 - X_1)^n \qquad (1)$$

where X_i is the mole fraction of component i, and the A_n are functions of temperature and pressure only. Suppose now that solutions a and b flow together to form mixture

m, and that the mass flow rates are $\dot{m}_a, \dot{m}_b$, and $\dot{m}_m = \dot{m}_a + \dot{m}_b$ respectively. The steady state heat evolution $\delta\dot{H}$ is given by:

$$\delta\dot{H} = \Delta\bar{H}_M(m)(\dot{m}_m/\bar{M}_m) - \Delta\bar{H}_M(a)(\dot{m}_a/\bar{M}_a) - \Delta\bar{H}_M(b)(\dot{m}_b/\bar{M}_b) \tag{2a}$$

where $\Delta\bar{H}_M(i) = \Delta\bar{H}_M[X_1(i)]$ and $\bar{M}_i = X_1(i)M_1 + X_2(i)M_2$ is the average molecular weight of solution i. Since $\dot{m}_i = \rho_i\dot{V}_i$, where ρ_i is the density of solution i and $\dot{V}_i$ is the volumetric flow rate, the expression:

$$\delta\dot{H} = [\delta\hat{H}(a)(1 + \rho_b\dot{V}_b/\rho_a\dot{V}_a)^{-1} + \delta\hat{H}(b)(1 + \rho_a\dot{V}_a/\rho_b\dot{V}_b)^{-1}]\dot{m}_m \tag{2b}$$

is obtained, where $\delta\hat{H}(i) = [\Delta\bar{H}_M(m)/\bar{M}_m - \Delta\bar{H}_M(i)/\bar{M}_i]$ This relation allows comparisons to be made between integral and differential heats.

For polymer solutions the appropriate measure of composition is the volume fraction of polymer v_2; in accord with usual practice let:

$$\Delta H_M = n_1 v_2 \sum_{j=0} B_j v_2^j \tag{3}$$

so that

$$\bar{H}_1 - \bar{H}_1^0 = \bar{H}_1^R = \sum_{j=0} (B_j - B_{j+1})(j+1)v_2^{j+2}$$

The parameters $\kappa_{j+1} = (B_j - B_{j+1})(j+1)/RT$; hence:

$$\kappa = \bar{H}_1^R/RTv_2^2 = \sum_{j=0} \kappa_{j+1} v_2^j \tag{4}$$

Upon mixing solutions a and b the steady state heat:

$$\delta\dot{H} = \dot{n}_1(a)\sum_{j=0} B_j[v_2(m)^{j+1} - v_2(a)^{j+1}] + \dot{n}_1(b)\sum_{j=0} B_j[v_2(m)^{j+1} - v_2(b)^{j+1}] \tag{5}$$

is produced. We ignore the small volume change on mixing to give:

$$v_2(m) = v_2(a) + \Delta v = v_2(b) - \Delta v$$

and

$$\dot{n}_1(i) = v_1(i)\dot{V}_i/\bar{V}_1$$

where $\bar{V}_1$ is the molar volume of the solvent. The volumetric flows $\dot{V}_a$ and $\dot{V}_b$ are as nearly equal as possible in our apparatus, but for illustrative purposes let $\dot{V}_b = r\dot{V}_a$. Then it may be shown that equation (5) yields:

$$\delta\dot{H} = (1 + r)RT(\dot{V}_a/\bar{V}_1)(\Delta v)^2\kappa_{\mathrm{app}} + 0[(1 - r)\Delta v] + 0[(\Delta v)^4] \tag{6}$$

where

$$\kappa_{\mathrm{app}} = \kappa_1 + (3/2)\kappa_2 v_2(m) + ---$$

and where higher terms are of orders indicated. For $r \simeq 1$ and for small Δv we have

$$\delta\dot{H} = (RT\dot{V}_m/\bar{V}_1)(\Delta v)^2\kappa_{\mathrm{app}} \tag{7}$$

where $\dot{V}_m = 2\dot{V}_a = 2\dot{V}_b$.

EXPERIMENTAL

Apparatus

Mixing unit and jacket. The flow microcalorimeter is of a design inspired by the instrument of Stoesser and Gill[7]. The twin calorimeter units, depicted in *Figure 1a*, are as similar to one another in all details as it was possible to make them. The main body of each consists of a pair of copper plates 7.8 cm in diameter and 0.6 cm thick in which is machined a spiral groove. Gold tubing (1.4 mm o.d., 1.0 mm i.d., 1 m long) fits closely into the groove, and is sandwiched between the two plates. A Y-junction entry port and mixing chamber, which is welded to one end of this tubing, is positioned in a hole drilled in the centre of the copper plates. The two plates are securely fastened to one another with four machine screws.

A bifilar spiral of 40 gauge, silk wound and enamelled manganin wire of about 200 Ω resitance serves as the heater in each calorimeter unit. This wire is positioned next to the gold tubing, and is fixed to one of the copper plates with epoxy glue.

Each mixing unit is suspended inside an adiabatic jacket with monofilament nylon fishing line, as shown in *Figure 1b*. This jacket is an axially split cylinder which allows

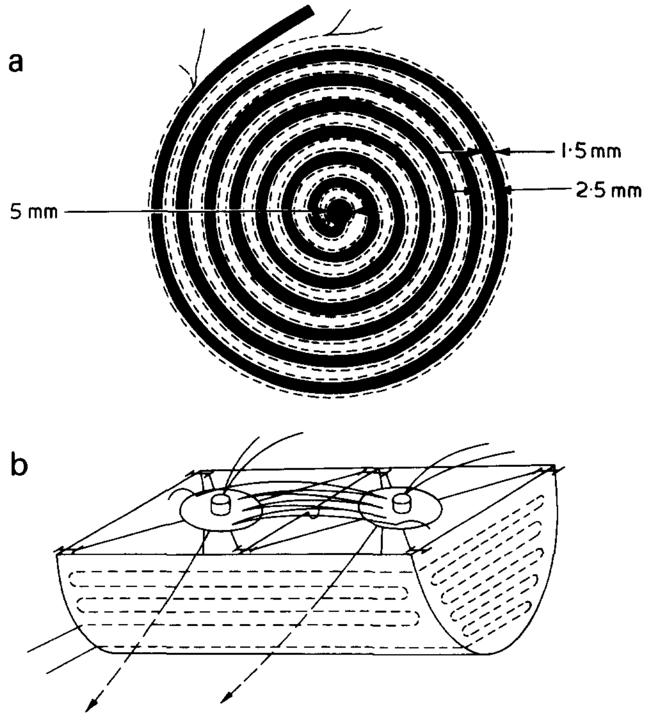

Figure 1 (a) The heat exchanger; (b) schematic showing the arrangement of the twin heat exchangers in the adiabatic shield

ready access to the calorimeter units. The two units are separated by a stainless steel wall of ~1 mm thickness, through which passes the several wires of a 52 junction copper–constantan thermocouple. Cigarette paper is used to electrically insulate the thermocouple from the jacket. The junctions of this thermocouple are inserted into drilled holes in the copper plates (13 to a side) and are secured with epoxy glue. Short sections of heat-shrinkable tubing are used to electrically insulate the junctions from the copper plates. (We attempted to use several different types of insulation material for this purpose, but none worked as well as the heat-shrinkable tubing.)

The adiabatic jacket is 14 cm in diameter and 28 cm long, thus providing a 1/1, length/diameter chamber for each calorimeter unit. An 8 junction thermocouple runs between the paired copper plates and the inside of the jacket. Junctions are insulated with heat-shrinkable tubing, and are secured with epoxy glue in drilled receptacles as previously described. The outside of the jacket is painted with enamel, and is wound with a manganin wire heater of about 1500 Ω resistance.

The adiabatic jacket and contents are suspended in a copper submarine which is thermostatically controlled by means of a water bath. The bath temperature is controlled (±0.002°C short term ±0.01°C long term) by a mercury contact thermoregulator.

Flow system. Fluid is delivered to the mixing units from mechanically driven syringes via Teflon tubing. The driving unit consists of four matched stainless steel syringes of ~12 cm^3 volume that are driven by a variable speed d.c. motor (Bodine NSF-34RJ). The flow paths from the syringes are controlled by 3-way valves (Hamilton Co.). Flow lines enter the calorimeter through copper pipes which support the submarine vessel. The Teflon lines make two turns around the adiabatic jacket for thermal equilibration, then pass through the jacket and connect to the two arms of the gold Y-junction mixing ports in each of the calorimeter twins. Thus the two units are similar in all respects, including the flow system.

Upon exit from the mixing units the flow path carries the fluid out of the submarine to a waste container or to a specially designed container for gravimetric measurement of flow rates.

Thermocouples. The thermocouples are constructed from enamelled 20 gauge constantan and 30 gauge copper wires (Leeds and Northrup Co.). The ratio of cross-sectional areas of the constantan to copper is about 10, which is somewhat less than the ratio 21.4 recommended by White[8]. Thermocouples with the latter size ratio are very difficult to construct. The ends of the various wires were scraped clean of enamel, the copper was crimped over the slightly flattened end of the constantan, and the junctions were then soldered together.

All electrical connections in the thermocouple circuits, apart from the copper–constantan junctions themselves, are made with low thermal solder. The output from the 52 junction thermocouple is amplified (Keithley Model 148 Nanovoltmeter) and displayed on a strip chart recorder (Honeywell Electronik 194). The operator uses this record to guide the manual adjustment of the heating rates in the calorimetric units.

The output from the 8 junction thermocouple, which is generated by a temperature difference between the copper plates and the adiabatic jacket, is amplified (Keithley Model 149 Milli-Microvoltmeter) and is then utilized to control the jacket heating when necessary. The signal from the voltmeter controls a relay, which switches the current to the jacket heater from adjustable high to low values.

Heater circuit. Two identical power sources (Power Designs Model 5005S), operated in the constant current mode, supply direct current to the various circuits of the instrument as required. The paired calorimeter units are each wired in series with a 120 kΩ variable resistor, but are parallel to one another and are powered by one of the constant current power supplies. A 5 kΩ resistor is connected in parallel to one of the 120 kΩ variable resistors which controls the power to the working calorimeter unit. A four-terminal 10 Ω resistor (Leeds and Northrup Co.) may be connected in series to either one or the other of the heaters by a low thermal connector, and is used to calibrate the resistances of the heaters. The variable resistors are adjusted manually to balance the heating rates in the calorimeter units, and the voltage drops across the 4-terminal heaters are measured potentiometrically (Leeds and Northrup Type K-5 Potentiometer and 9834-1 DC Null Detector). A standard cell (The Eppley Lab., Inc.) is used to calibrate the potentiometer.

The remaining power supply provides direct current to the jacket heater. Power from this unit is also used for a capsule-like platinum resistance thermometer (Minco Products, Inc.) which is positioned in a receptacle attached to the outside of the adiabatic jacket. A 100 Ω low temperature coefficient resistor is connected in series with the thermometer to determine the resistance of the thermometer potentiometrically. The resistance is translated into temperature of the jacket by means of the manufacturer's calibration. The block diagram of the calorimeter units with measurement and control systems is shown in *Figure 2*.

Materials

Solvents. Spectroquality reagents n-hexane, cyclohexane, benzene, and toluene from Matheson, Coleman, and Bell were used without further purification. The manufacturer reports 99+ mol % purity for the Spectroquality solvents. Reagent quality n-butyl acetate was used without further purification.

Polyisobutylene (PIB). Polyisobutylene was obtained by fractionation of Enjay Vistanex-LMMS from a 0.8% solution in benzene at 30°C using methanol as the precipi-

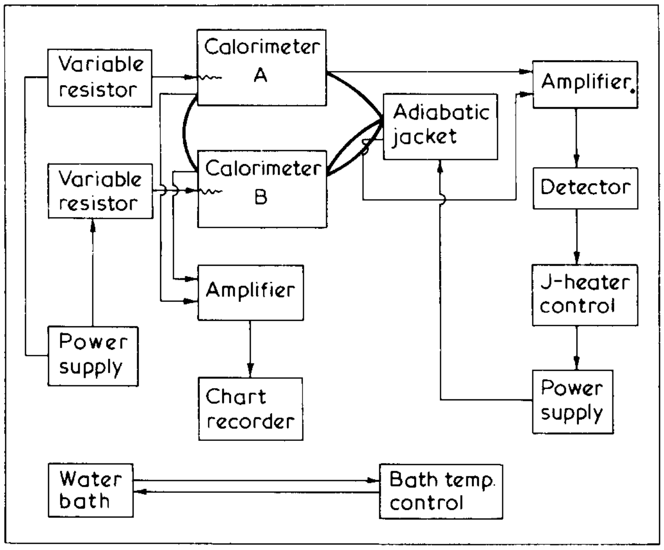

Figure 2 Schematic of the electrical control and measurement systems

tant. The first fraction was discarded and the second, third, and fourth fractions were pooled and retained. The solution remaining in the dilute phase after the fourth precipitation contained material of low molecular weight and was discarded. The viscosity-molecular weight of the fractionated polymer was not determined but is estimated[9] to be 4×10^4.

Polystyrene (PS). Polystyrene obtained from the Pressure Chemical Company was used without fractionation. The sample was characterized by $M_w/M_n < 1.06$ and the molecular weight was 20400.

Operation

Solutions *a* and *b* of differing concentrations were delivered to one of the calorimeter units, while mixtures of the two were delivered to the dummy unit from the mechanically driven syringes. As the solutions enter the Y-junction chambers, the heat of mixing generates a temperature difference between the two calorimeter units. The course of this thermal imbalance was observed on the strip chart recorder, and the operator manually adjusted the 120 kΩ variable resistor which is in series with the working calorimeter heater so as to nullify the temperature difference. The heating rate in the dummy unit was left constant during this adjustment. Steady state was generally achieved after a few trial settings and maintained for at least 15 min before the run was considered to be satisfactory. Similar measurements were obtained by delivering identical mixtures to both calorimeter units. The difference between the 'reaction' heat effect and 'blank' heat effect gives the net heat of mixing. The flow system was cleaned between runs involving different concentrations by washing with solvent.

The flow rate is determined from the weight of fluid discharged from the outlet during a timed interval. The net heat effect ΔP_{net} is divided by the mass flow rate, $\dot{m}$, to give the enthalpy per unit mass $\hat{H}$ (specific enthalpy). This quantity may be converted to volumetric or molar units by multiplication with the solution density or average molecular weight respectively.

At 25°C we generally found that the best reproducibility was achieved when the jacket heater was not used. The temperature of the jacket, when left to drift naturally, never departed from that of the mixing units by more than a few millidegrees. The calorimeter must, of necessity, have a heat leak; the natural rate of conduction was apparently more reproducible than an artificial one.

Determination of the heat capacity ratio C_1/C_2

For exothermic heats of mixing it is necessary to know the ratio C_1/C_2 of heat capacities of the two heat exchangers. To determine this ratio the calorimeter system was maintained at constant temperature for at least 24 h–until the potential generated by the 52 junction thermocouple was essentially null. After the equilibrium state was achieved, the power supply to the two calorimeters was turned on to supply constant power to both units. The temperature difference generated by the electrical heating was balanced by adjusting the 120 kΩ variable resistors connected in series with the respective heaters of the mixing units so as to reattain equal temperatures. When the steady state persisted for at least 15 min or longer, the voltage drops across the heaters of each calorimeter unit were measured potentiometrically, and the power supplied to each unit was calculated. The ratio of the electrical power to the two units yields the ratio of heat capacities $C_1/C_2 = 1.017$.

Table 1 Differential enthalpy of mixing n-hexane and cyclohexane at 25°C

Mole fraction of n-hexane				$\delta\bar{H}$(J/mol)	
Solution a	Solution b	Mixture	Runs	This work	McGlashan*
0.580	0.383	0.486	3	8.143	7.66
0.216	0.106	0.160	3	5.107	4.75
0.383	0.216	0.292	2	8.315	7.88
0.713	0.853	0.781	1	2.831	3.13

* Ref 10

RESULTS

Cyclohexane–n-hexane

Measured molar differential enthalpies of mixing n-hexane and cyclohexane solutions are listed in *Table 1*. The data recorded in column five are averages of separate measurements, the number of which is given in column four of the same table. Corresponding differential enthalpies calculated from reported integral enthalpy data are given in column six. The entries in this column were calculated from the empirical equation:

$$\Delta\bar{H}_M = X_2(1 - X_2)[866.10 - 249.4(X_2 - X_1) + 97.0(X_2 - X_1)^2 - 31.8(X_2 - X_1)^3] \tag{8}$$

given by McGlashen and Stoekli[10] with use of equation (2b). Volumes were taken to be additive, and densities of the pure liquids at 25°C were taken from the literature[11,12]. Differences between measured differential enthalpies and those calculated from the integral data do not exceed 9.5%.

The magnitude of the differences between measured and calculated $\delta\bar{H}$ is not as large as it might at first appear. In the first place, the differential enthalpies are about two orders of magnitude smaller than the integral enthalpies at comparable concentrations. In consequence, values of $\delta\bar{H}$ calculated from the integral data are subject to an estimated uncertainty of 2.2 J/mol–more than enough to account for the discrepancy. On the other hand, one may derive an empirical equation for $\Delta\bar{H}_M$ from the measured $\delta\bar{H}$. This has been done using our measured differential enthalpies by solving four simultaneous equations for the constants A_n of equation (1) used in conjunction with equation (2), with the result:

$$\Delta\bar{H}_M = X_2(1 - X_2)[821.1 - 307.8(X_2 - X_1) + 191.4(X_2 - X_1)^2 + 18.3(X_2 - X_1)^3] \tag{9}$$

Values of $\Delta\bar{H}_M$ calculated by means of this equation fall within 6.2% of those calculated from McGlashen's and Stoeckli's data, equation (8).

On the basis of these comparisons, we are satisfied with the accuracy of the flow microcalorimeter. At the time of design, order of magnitude estimates of the heat effects we anticipated measuring led to the conclusion that $\delta\bar{H}$ could be determined with about 10% accuracy. Values of κ_1 derived from the data are of course subject to similar limits of uncertainty. It appears that the calorimeter is some-

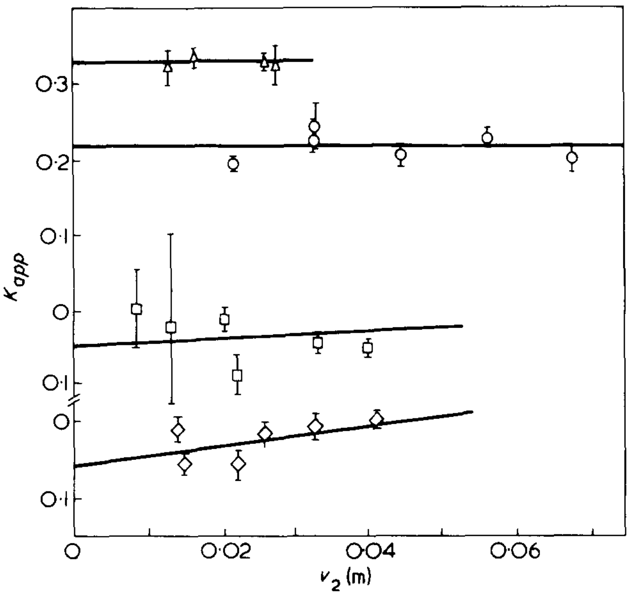

Figure 3 The apparent enthalpy parameter κ_{app} at 25°C as a function of the volume fraction of polymer in the mixture $\nu_2(m)$ for the systems: polystyrene (PS)–cyclohexane (△); polyisobutylene–benzene (○); and PS–*n*-butyl acetate (◇); and κ_{app} at 40°C for PS–toluene (□). Error bars represent average deviations for three or more runs of given concentration

Table 2 Comparison of values of the enthalpy parameter obtained by various methods: PIB–benzene at 25°C

Method	κ_1
Calorimetry (differential method, this work)	0.22
Calorimetry (integral method)[a]	0.21
Osmotic pressure[b]	0.19
Osmotic pressure[c]	0.34
Intrinsic viscosity[d]	0.15
	0.31
	0.19
Precipitation temperature[c]	0.65

[a]Ref 3; [b]ref 13; [c]ref 14; [d]ref 15, see text

what more accuracy than these preliminary estimates suggested. On this basis, a conservative estimate of the overall uncertainty of subsequent reported data is in the range 5–10%.

Polymer solutions

The apparent enthalpy parameters calculated from experimental data for the systems PIB–benzene, PS–cyclohexane, PS–toluene, and PS–n-butyl acetate solutions are shown plotted against volume fractions of the respective polymers in *Figure 3*. The enthalpy parameters

$$\kappa_1 = \lim_{\nu_2 \to 0} \kappa_{app}$$

are found from the intercept of the least-squares straight lines to be 0.22 ± 0.01, 0.33 ± 0.01, –0.05 ± 0.01, and –0.06 ± 0.02 for these systems respectively (reported errors are standard deviations of intercepts). We do not suggest that undue significance be attached to the concentration dependence of κ_{app}.

We observed an abrupt drop of κ_{app} for PS–cyclohexane solutions above volume fractions of about 2.8%. This behaviour was presumed to be caused by phase separation occurring in the pumping syringes which are not thermostatted. These data are not reported.

COMPARISON WITH OTHER DATA

PIB–benzene

Values of the enthalpy parameter κ_1 for PIB–benzene previously obtained by others at 24.5°–25.0°C are summarized in *Table 2*. Results from flow and batch microcalorimetry[3] are identical within errors of measurements. The value of κ_1 obtained from the osmometric data reported by Flory and Daoust[13] is in closer agreement with calorimetric results than is that obtained by Krigbaum and Flory[14].

Intrinsic viscosity data for this system have been collected over wide ranges of molecular weight and temperature, and have been analysed by Flory and Fox[15] to give the entropy parameter ψ_1 and the theta temperature. At $T = \theta$, $\kappa_1 = \psi_1$; this result is included in *Table 2*. We have reanalysed the same viscosity data to deduce ψ_1 and θ by the use of both the modified Flory equation[16] and the Flory–Fisk equation[17], and find $\psi_1 = 0.31, \theta = 297.2$K and $\psi_1 = 0.19, \theta = 297.0$K respectively. The $\kappa_1 = \psi_1$ parameters deduced from these alternative theories are likewise included in *Table 2*.

The value for ψ_1 deduced from *UCST* measurements[14] is much greater than the similar values obtained by other methods, as is revealed in *Table 2*. This is found for PIB–benzene and, as will be seen, for PS–cyclohexane as well. On the basis of subsequent discussion, this discrepancy seems to result from neglect of the concentration dependence of the mixing parameters, and presumably could be ameliorated on resorting to recent theory. However, we have not undertaken fresh analysis of these data.

PS–cyclohexane

The enthalpy parameter κ_1 obtained by the authors for the PS–cyclohexane system is compared with the corresponding quantity determined by other methods in *Table 3*. The value for κ_1 deduced from osmotic pressure measurements[18] is in fair agreement with the calorimetric data. The intrinsic viscosity data analysed by the original Flory–Fox equation[19] yields a smaller value (0.13) than is obtained from other theoretical relations. Following the procedure used for the previous system, i.e. by application of the modified Flory equation and the Flory–Fisk equation, we calculate ψ_1 to be 0.27 with use of the former equation, but are unable to reliably estimate ψ_1 with the latter owing to pronounced curvature in the $z/M^{1/2}$ vs. $1/T$ plot.

Recent measurements on the precipitation temperatures of PS–cyclohexane solutions have been reported by Koningsveld and coworkers[20]; ψ_1 is found to be 0.30 by the use of theory which takes the concentration dependence of the interaction parameter into consideration.

Table 3 Comparison of values of the enthalpy parameter obtained by various methods: PS–cyclohexane at 25°C

Method	κ_1
Calorimetry (differential method, this work)	0.33
Osmotic pressure[a]	0.37
Intrinsic viscosity[b]	0.13
.	0.29
Precipitation temperature[c]	0.31
Precipitation temperature[d]	1.09
Light scattering[e]	0.31
Sedimentation-diffusion equilibrium[f]	0.23

[a]Ref 18; [b]ref 19, see text; [c]ref 20; [d]ref 21; [e]ref 22; [f]ref 22

Table 4 Comparison of values of the enthalpy parameter obtained by various methods: PS–toluene at 40°C

Method	κ_1
Calorimetry (differential method, this work)	−0.05
Osmotic pressure[a]	~0
Osmotic pressure[b]	−0.03
Osmotic pressure[c]	−0.15
Viscosity[d]	+0.06
Viscosity[e]	+0.06
Vapour pressure equilibrium[f]	~0
Sedimentation–diffusion equilibrium[g]	~0
Calorimetry (integral method, 25°C)[h]	−0.1
Calorimetry (integral method, 30°C)[i]	−0.05
Calorimetry (integral method, 25°C)[j]	−0.08
Calorimetry (integral method, 25°C)[k]	−0.27
Calorimetry (integral method, 25°C)[l]	−0.14

[a] Ref 30; [b] ref 32; [c] ref 23; [d] ref 24; [e] ref 19; [f] ref 25; [g] ref 22; [h] ref 6; [i] ref 5; [j] ref 4; [k] ref 2; [l] ref 1

From ψ_1 and θ = 307K, we find κ_1 to be 0.31 at 25°C. This value is in good agreement with the calorimetric result, but is far different from the value 1.09 first reported by Schultz and Flory[21].

Light scattering and sedimentation–diffusion equilibrium data reported by Scholte[22] have been used to estimate ψ_1. The quantity χ characterizing the interaction between polymer segments and solvent molecules was obtained by Scholte on application of the Flory–Huggins equation. The value χ_1 at infinite dilution of polymer was obtained by extrapolation. Since the Flory–Huggins equation is not applicable to dilute solutions, the evaluation of the enthalpy parameter from the temperature dependence of χ_1 is not strictly correct. Nevertheless, values of χ_1 at temperatures close to the θ point of the PS–cyclohexane system were used to calculate κ_1 from the relationship $\kappa_1 = -T(\partial\chi_1/\partial T)$, and ψ_1 is subsequently obtained from $\psi_1 - \kappa_1 = 1/2 - \chi_1$. This method is subject to error in the estimation of both κ_1 and ψ_1 owing to use of the Flory–Huggins equation, and to the necessity of taking small difference between large numbers to compute the temperature coefficient of χ_1. Thus, we report κ_1 as 0.31 ± 0.03 from light scattering data and 0.23 ± 0.05 from sedimentation–diffusion equilibrium data.

PS–toluene

The PS–toluene system has been much investigated in recent years to probe for specific interactions between polymer and solvent[1,2,4–6,22–32]. Values of the enthalpy parameter have been obtained by many different methods, and these other results are summarized in *Table 4*. The enthalpy parameters deduced from osmotic pressure measurements are consistent with those obtained calorimetrically.

Direct comparison of the value of κ_1 obtained by us with the integral calorimetric method at 40°C is not possible. However, several groups have reported results for κ_1 at different temperatures. These values are also included in *Table 4* for reference purposes.

The positive value for κ_1 obtained from viscosity data[24] is subject to doubt attending theoretical analysis of chain dynamics. The parameters ψ_1 and κ_1 determined from viscosities are subject to the uncertainties mentioned by Fox and Flory[19], and should be judged to be only approximate.

From vapour pressure equilibrium[25], the interaction parameter χ_1 is found to be temperature independent; therefore $\kappa_1 \sim 0$. Light scattering data reported by Scholte[22] yields a positive enthalpy parameter from the temperature dependence of χ_1. The large scatter of data obtained by Scholte at low concentrations is presumably due to application of the Flory–Huggins equation for dilute solutions. The value of χ_1 deduced from the results of sedimentation–diffusion equilibria reported by the same author are essentially temperature independent and thus $\kappa_1 \sim 0$.

PS–n-butyl acetate

Other thermodynamic data with potential to corroborate our result for the PS–n-butyl acetate system are not available. However, the *UCST* and *LCST* of infinite molecular weight PS with n-butyl acetate may be determined to be approximately 170K and 497K by extrapolation from the *UCST* and *LCST* of PS with the series methyl acetate, ethyl acetate, and n-propyl acetate obtained by Saeki *et al.*[33]. This is by no means an accurate method to evaluate the *UCST* and the *LCST*; nevertheless, the *LCST* obtained by extrapolation is quite close to that measured by Bataille[34]. If the enthalpy parameter κ_1 changes linearly with temperature, values of κ_1 for PS–ethyl acetate and PS–n-propyl acetate are approximately null at room temperature. Hence, it is reasonable to predict $\kappa_1 \sim 0$ at 25°C for PS–n-butyl acetate. This gross estimate does not contradict the small negative value (−0.06) obtained calorimetrically.

DISCUSSION

Assessment of the calorimeter

The measurements we have reported on n-hexane–cyclohexane mixtures were undertaken to assess the reliability of the calorimeter. This system was chosen for study for the reason that integral enthalpies have been measured in several different laboratories,and the results agree within 1% according to McGlashan and Stoeckli. They recommend this mixture for the purpose to which we have put it. While our calorimeter used differentially does not reproduce with accuracy the best integral data, we have established that it is reliable to within 5–10% for small heats. (Integral heats could be measured with the instrument described, even though we have not yet made such measurements for the obvious reason that accurate measurement of a large heat effect does not guarantee precision on the small.) In favourable cases, i.e. for polymer solutions with large positive κ_1, it appears that flow calorimetry is as accurate as batch calorimetry, and that viscous heating in the flow system is inconsequential.

Second virial coefficients[35]

We now consider a slightly different topic; that is, the application of calorimetric data to theories of the second virial coefficient. According to the original Flory–Krigbaum (FK) theory[36] the second virial coefficient A_2 is given by:

$$A_2 = (\bar{v}^2/\bar{V}_1)\psi_1(1 - \theta/T)F(z)$$

where $\bar{v}$ is the specific volume of the polymer and z is the interaction parameter. The function $F(z)$ is a monotonically decreasing function of z, and is calculated from the binary cluster integral for molecules. Several alternatives have been proposed to improve on the FK theory. The first of those considered here for illustrative purposes is the Flory–

Table 5 Comparison of theoretical and experimental second virial coefficients for PIB–benzene

$M^{1/2} \times 10^{-2}$	T(K)	$A_2 \times 10^5$ (cm^3 mol/g^2)			
		FKO-m	CM	KY	EXP*
3.18	293	−4.98	−4.72	−5.15	−7.18
	303	5.28	4.80	5.39	8.33
	313	12.97	11.32	12.65	19.4
4.37	293	−5.67	−4.93	−6.08	−7.14
	303	4.78	4.68	4.66	7.78
	313	10.79	10.78	10.06	17.3
4.54	293	−5.76	−4.97	−6.16	−6.67
	303	4.79	4.66	4.68	7.21
	313	10.35	10.78	9.58	15.9
8.43	293	−6.40	−5.73	−7.06	−7.03
	303	4.06	4.30	3.79	7.04
	313	8.72	9.24	7.79	15.1

* Ref 14

Table 6 Comparison of theoretical and experimental second virial coefficients for PS–cyclohexane

$M^{1/2} \times 10^{-2}$	T(K)	$A_2 \times 10^5$ (cm^3 mol/g^2)			
		FKO-m	CM	KY	EXP*
2.247	303	−3.35	−3.51	−3.37	−2.76
	313	3.86	4.45	3.68	6.34
	323	8.19	10.49	7.47	13.30
3.536	303	−3.72	−3.66	−3.83	−2.45
	313	3.91	4.25	3.73	5.78
	323	8.37	9.56	7.67	11.63
5.992	303	−3.89	−3.96	−4.04	−1.98
	313	4.22	3.89	4.10	5.28
	323	8.59	8.02	7.91	10.0
7.523	303	−4.00	−4.16	−4.18	−1.78
	313	4.20	3.70	4.07	5.25
	323	8.57	7.26	7.89	9.22

* Ref 18

Krigbaum–Orofino theory[37] as modified by Stockmayer[16] (FKO-m), for which:

$$A_2 = (\bar{v}^2/\bar{V}_1)\psi_1(1 - \theta/T)(5.73\bar{z})^{-1}\ln(1 + 5.73\bar{z})$$

with $\bar{z} = z/\alpha^3$; the expansion factor α of the radius of gyration is calculated[16] from $\alpha^5 - \alpha^3 = (134/105)z$. The theory of Casassa and Markovitz (CM) gives[38]:

$$A_2 = (\bar{v}^2/\bar{V}_1)\psi_1(1 - \theta/T)\,[1 - \exp(-5.68\bar{z})]/5.68\bar{z}$$

As a last example, the Kurata–Yamakawa (KY) theory[35,39] yields:

$$A_2 = (\bar{v}^2/\bar{V}_1)\psi_1(1 - \theta/T)\,[1 - (1 + 3.903z)^{-0.4683}]/1.828z$$

In all of the above:

$$z = (4/3^{3/2})C_M\psi_1(1 - \theta/T)M^{1/2}$$

with

$$C_M = (3^3/2^{5/2}\pi^{3/2})(\bar{v}^2/\bar{V}_1N_a)(M/\langle r^2\rangle_0)^{3/2}$$

For application of these equations, several pieces of information are required. Specific volumes for PIB[9], nonglassy PS[40], benzene[9], and cyclohexane[12] were taken from sources indicated. Chain dimensions for PIB were taken from the work of Kunst[41]; those for PS were given by Fox and Flory[19]. These parameters, together with $\psi_1 = 0.22$, $\theta = 297.5$K for PIB–benzene and $\psi_1 = 0.32$, $\theta = 307.2$K for PS–cyclohexane, yield the calculated second virial coefficients listed in *Tables 5* and *6*. A quick perusal of these Tables discloses that none of the theories considered has sufficiently large temperature dependence to match that of the experimental data. Nor do they seem to reproduce the molecular weight dependence of the experimental A_2 at fixed temperature. Although we have not investigated the influence of temperature dependence of ψ_1 on theoretical values of A_2, it must be concluded that over a range of 20°C such dependence will not drastically alter the general lack of agreement between theory and experiment. The resolution of these discrepancies is most likely to be found in refined estimates of the segmental distribution function.

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