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The Determination of Thermodynamic Properties of Polymer Solutions by Finite-Concentration Gas Chromatography

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ABSTRACT

Although the technique of gas chromatography has been widely used to study polymer properties and to obtain information on polymer solution thermodynamics, few workers have extended their results beyond infinite dilution of solvent. Finite-concentration gas chromatography has been used to study several poly(dimethylsiloxane)-solvent systems at 25°C. The results are in good agreement with those obtained by traditional vapor sorption methods. A comparison of the various available techniques has been made, and the advantages and disadvantages of each are discussed.

INTRODUCTION

The technique of gas chromatography (GC) has been used to study a number of polymer properties, such as glass transition and melting temperatures, crystallinity, and diffusion coefficients [1]. In 1969 Smidsrød and Guillet [2] were the first to use GC to measure thermodynamic properties such as activity coefficients and enthalpies of solution. Since then a considerable amount of work has been done using GC

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to study the thermodynamics of polymer systems. However, the vast majority of this work has been limited to infinite dilution of solvent.

Also in 1969, Conder and Purnell, in a series of papers [3-6], developed the mathematical basis for the use of GC at finite solvent concentrations and showed that the method gave results that agreed with traditional static methods. It is therefore, perhaps, surprising that few workers have employed the technique.

Brockmeier, McCoy, and Meyer [7-9] were the first to adapt the work of Conder and Purnell to the study of polymers, obtaining data on several polymer-solvent systems over concentrations ranging up to approximately 0.5 weight fraction. Chang and Bonner [10] measured the activity of benzene-poly(ethylene oxide) solutions at 70°C and found fair agreement with vapor sorption results. Aspler and coworkers [11, 12] used finite-concentration GC to study the effect of water on a number of materials, while Lau et al. [13] investigated polybutadiene solutions in benzene and cyclohexane at temperatures from 60 to 100°C. However, apart from these, the technique seems to have been generally ignored in favor of other experimental methods.

Several methods are available for the measurement of thermodynamic properties of solutions [14]. Those based on measurement of solution virial coefficients (e.g., osmotic pressure or light scattering) are applicable only to dilute solutions—the opposite end of the concentration range from that in GC—and will not be considered further here. The technique most comparable with chromatographic experiments is that of vapor sorption. A number of types of apparatus are available [15], the most commonly used being based around vacuum microbalances or other sorption detectors.

Finite-concentration GC results may be obtained in a variety of ways [16]. The work to be described in this paper has been performed using the "elution on a plateau" or "step and pulse" method. This involves the equilibration of the chromatograph column with a mixed carrier-solvent vapor stream of known constant composition, followed by the injection of a small quantity of solvent as in a conventional GC experiment. This method avoids the need for exacting detector calibrations and also allows relatively straightforward calculation of results.

The properties of poly(dimethylsiloxane) (PDMS) in a number of solvents have been investigated around room temperature by vapor sorption. An apparatus to perform finite-concentration GC measurements has been constructed and used to study solutions of PDMS in benzene, cyclohexane, and hexane at 25°C. The results obtained have been compared to those published previously, and an assessment of the advantages and disadvantages of the various techniques has been made.

EXPERIMENTAL

Apparatus

The apparatus was a modified form of that used by Conder and Purnell [6] and that of Brockmeier et al. [8]. It is shown schematically in Fig. 1.

A stream of pure helium controlled by a Hewlett-Packard HP6710 mass flow controller was split into two lines, each controlled by a Matheson Products 600 fine needle valve and rotameter combination. The gas lines were constructed from 1/8 in. o.d. copper tubing. When used with pure helium, i.e., the conventional infinite dilution GC experiment, Valve B was closed to isolate the saturator. For a mixed carrier gas stream, helium was allowed to flow through the saturator which consisted of a 1-L round-bottom flask into which helium flowed through a gas diffuser. A heating mantle maintained the solvent in the flask just below its boiling point to prevent variations in flow rate due to bubbling. The mixed helium-solvent vapor stream then passed through a condenser through which was passed accurately thermostatted water. The condenser was packed with glass beads to increase its effective path length. The total pressure at the saturator was measured to ±0.25 torr using a mercury manometer. This, along with the

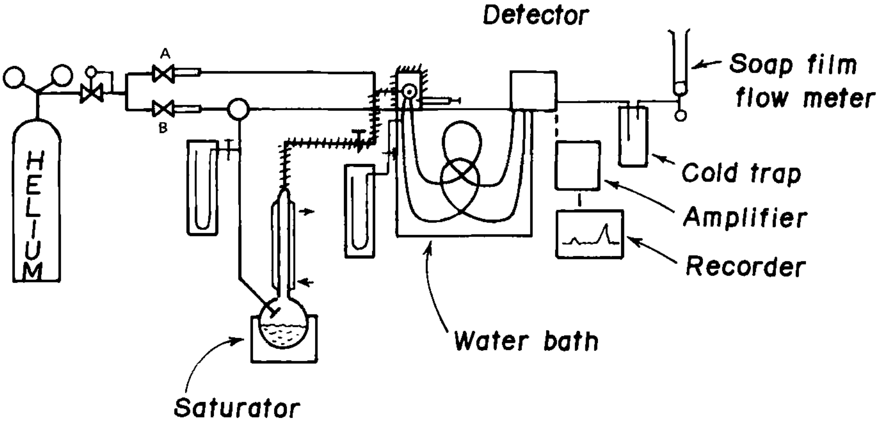

FIG. 1. Schematic diagram of finite-concentration gas chromatography apparatus.

saturated vapor pressure of the solvent at the condenser temperature (controlled to ±0.02°C), allowed calculation of the gas stream composition. Preliminary trials showed the resulting gas flows to be fully saturated within the experimental error of the method (98 ± 2%) [17].

The apparatus thus allowed two ways of varying the solvent concentration in the gas stream. First, the temperature of the saturator condenser could be changed to vary the partial pressure of the solvent. Second, the mixed stream could be combined with a flow of pure helium, both Valves A and B being used in this case.

To ensure that no solvent condensed between the saturator and the columns, connecting tubing was wrapped with heating tape and, together with the injection port which was constructed from a brass block, maintained at a temperature well above that of the columns. A water bath was used to thermostat the columns to within ±0.01°C, and the temperature was monitored with precision mercury-in-glass thermometers.

A twin-channel Gow Mac 40-001 thermal conductivity detector was used to monitor the gas streams passing through the column packed with polymer-coated support and a reference column packed with uncoated support. The flow between the columns was controlled by a Nupro fine metering needle valve. The pressure at the inlet of the polymer-containing column was measured with a mercury manometer. To ensure that the solvent partial pressure remained constant, the pressure drop along the column was maintained within the usual limits, as suggested by Conder and Purnell [3-6]. The helium flow rate through the column was measured with a thermostatted soap bubble flow meter after condensing the solvent vapor in an acetone/solid carbon dioxide cold trap.

Procedure

Before commencing work at finite concentrations, a conventional GC experiment was performed. Samples of solvent, in the region of 0.01 to 0.05 μL, were injected into a stream of pure helium and the retention times measured to ±0.1 s with a stopwatch. All peaks obtained were symmetrical, and no dependence of retention time on flow rate or sample size in this range was detected. Air was employed as a marker to enable calculation of the gas hold-up correction.

The flow rates through Valves A and B were then set and the heating mantle switched on. When the column was equilibrated with the gas stream, the retention times of solvent and air were recorded, an average of five values within 1% usually being taken. As the concentration of solvent in the carrier became higher, larger sample sizes of up to 1.5 μL were required to give an adequate signal. Also, the recorded peaks became much broader, so that the retention times were determined by drawing tangents to the peaks on the chart paper. The precision of the retention times at the higher concentrations was 1.5-2%.

Materials

Since the saturated vapor pressure of the solvent is required for the calculation of results, high-purity compounds must be used. The benzene and cyclohexane were Aldrich HPLC-grade solvents of stated purity $\geq$ 99.9%. The n-hexane was a BDH Assured-Grade solvent of purity $\geq$ 99%.

The PDMS polymer was an OV101 gas chromatography stationary phase supplied by Chromatographic Specialities. Its intrinsic viscosity at 20°C, as measured by capillary viscometry, was 0.185 g/dm^3, corresponding to $\overline{M}_n$ = 31 000 [18].

The polymer was dispersed onto a 40-50 mesh Celite 545 AW solid support using chloroform as the solvent. Careful sample preparation was employed in order to calculate the polymer loading, and this was checked by exhaustive Soxhlet extraction with hot chloroform. Both methods gave the same result of 4.08 wt%, a total of 0.253 g of polymer being used.

DATA REDUCTION

The treatment of the elution on a plateau technique as developed by Conder and Purnell is summarized here. For a full discussion, the reader is referred to the original publications [3-6].

The primary datum measured in a GC experiment is the retention volume, V_N, given by

$$V_N = (t_r - t_m)F, \tag{1}$$

where t_r and t_m are the retention times for the solvent and an inert marker (air), respectively, and F is the carrier gas flow rate given by

$$F = \left(\frac{V_f}{t_f}\right)\left(\frac{P_A - P_W}{P_A}\right)\left(\frac{T}{T_F}\right)J_3^{\,2}, \tag{2}$$

where t_F is the time taken for a volume V_F to pass through the flowmeter at temperature T_F and atmospheric pressure P_A. T is the column temperature, P_W is the vapor pressure of water at T_F, and $J_3^{\,2}$ is a compressibility correction (see later).

Flow rates of mixed carrier-solvent streams must be corrected for the sorption effect [16], so that

$$F = \frac{F'(1 + k)}{1 + k(1 - \psi)}, \tag{3}$$

where F' is the flow rate calculated from Eq. (2) and ψ is the mole fraction of solvent in the carrier stream. The partition coefficient k is given with sufficient accuracy by $(t_r - t_m)/t_r$.

The approximate mole fraction of solvent in the carrier y_0 may be calculated from the saturated vapor pressure of solvent at the condenser temperature $P_1{}^0(T_s)$ and the total pressure in the saturator P_s according to

$$y_0 = P_1{}^0(T_s)/P_s. \tag{4}$$

The true mole fraction ψ is obtained by correcting y_0 by factors a, for gas phase nonideality, and j, for compressibility effects due to the pressure gradient in the column. These factors take the form

$$a = \frac{1 + k(1 - J_2{}^1 y_0)}{1 + k(1 - J_3{}^2 y_0)}\left[1 + \frac{2y_0 P_A B_{11}(1 - J_2{}^1 y_0)}{RT}\right] \tag{5}$$

$$j = J_3{}^2\left[\frac{1 + y_0{}^2 P_A B_{11}(J_3{}^2 - 1)}{RT}\right] \tag{6}$$

In Eqs. (5) and (6), B_{11} is the second virial coefficient of the solvent vapor at the column temperature. Also

$$J_n{}^m = \frac{n}{m}\left[\frac{(P_i/P_A)^m - 1}{(P_i/P_A)^n - 1}\right], \tag{7}$$

where P_i is the pressure at the column inlet. ψ is then given by

$$\psi = ajy_0. \tag{8}$$

Conder and Purnell showed that the partition isotherm for solvent between vapor and liquid phases is given by

$$\frac{\partial q}{\partial c} = \frac{jV_N}{v_s(1 - \psi)}, \tag{9}$$

where q and c are the solvent concentrations in the liquid and vapor phases, respectively, and v_s is the volume of polymer in the column. By integrating Eq. (9) and introducing the weight of polymer used, w, the concentration of solvent in the liquid, expressed as mol/(g polymer), may be calculated from

$$q = \frac{j}{w} \int_0^c \frac{V_N}{1 - \psi}\, dc. \tag{10}$$

The concentration of solvent in the vapor may be obtained by taking the first-order terms of a virial expansion

$$c = \frac{P_A \psi}{ajRT + \psi^2 B_{11} P_A}. \tag{11}$$

In the experiment, a series of measurements of V_N was made at varying solute concentrations. Evaluation of the integral in Eq. (10) was facilitated by fitting the data to a polynomial curve of the form

$$\frac{V_N}{1 - \psi} = \sum_0^n a_n c^n \tag{12}$$

and integrating the resulting polynomial equation analytically.

From the definition of q given above, it is clear that the weight fraction of solvent in the liquid phase is

$$W = \frac{qM_1}{1 + qM_1}, \tag{13}$$

where M_1 is the molecular weight of the solvent. The mean pressure in the column, P_m, is $P_A J_3{}^4$, so that the partial pressure of solvent P_1, is given by $P_1 = \psi P_m$.

Thus, knowing the saturation pressure at the column temperature P_1^0, the thermodynamic activity a_1 and activity coefficient Ω_1 may be calculated from

$$\Omega_1 = \frac{a_1}{W_1} = \frac{\psi P_m}{P_1^0 W_1}. \tag{14}$$

Note that Ω_1 represents an activity coefficient rationalized by weight fraction which is more advantageous when dealing with polymers than the mole fraction activity coefficients used with low molecular weight liquids [19].

In conformity with recent usage [20], the best concentration basis on which to analyze solution data is that of segment fraction ϕ,

$$\phi_1 = \frac{W_1\nu_1^*}{W_1\nu_1^* + (1 - W_1)\nu_2^*}, \tag{15}$$

where ϕ_1 is the segment fraction of solvent and ν^* represents the specific hard core volume. The Flory-Huggins interaction parameter may be calculated from

$$\chi^* = \frac{\ln(a_1) - \ln(\nu_2^*/\nu_1^*) - [1 - (M_1\nu_1^*/M_2\nu_2^*)]}{(1 - \phi_1)^2} \tag{16}$$

The superscript denotes that the interaction parameter is calculated in terms of segment rather than the sometimes used volume fractions, the latter values generally being ~0.1 lower.

When working at infinite dilution (i.e., ψ, c, W_1, etc. all zero), these expressions cannot be used and the equations normally employed in GC work must be used [1].

$$\ln \Omega_1^\infty = \ln\left(\frac{273.2RW}{P_1^0 M_1 V_N}\right) - \frac{P_1^0}{RT}(B_{11} - V_1^0), \tag{17}$$

$$\chi^{*\infty} = \ln \Omega_1 - \ln(\nu_2^*/\nu_1^*) - \left(1 - \frac{M_1\nu_1^*}{M_2\nu_2^*}\right). \tag{18}$$

RESULTS AND DISCUSSION

Plots of $V_N/(1 - \psi)$ versus vapor concentration as in Eq. (10) are shown in Fig. 2. In calculating the values, solvent vapor pressures were calculated from Antoine constants [21], and second virial coefficients were obtained from the experimental data compilation of Dymond and Smith [22]. Solvent densities and specific hard-core volumes were taken from the work of Flory et al. [23, 24], while those for the polymer were extrapolated from the work of Ashworth and Price [25] and that of Muramoto [26]. The values at 25°C are shown in Table 1.

Figure 2 shows that as the vapor concentration increases, the slope of the curve becomes increasingly steep. Since the evaluation of the

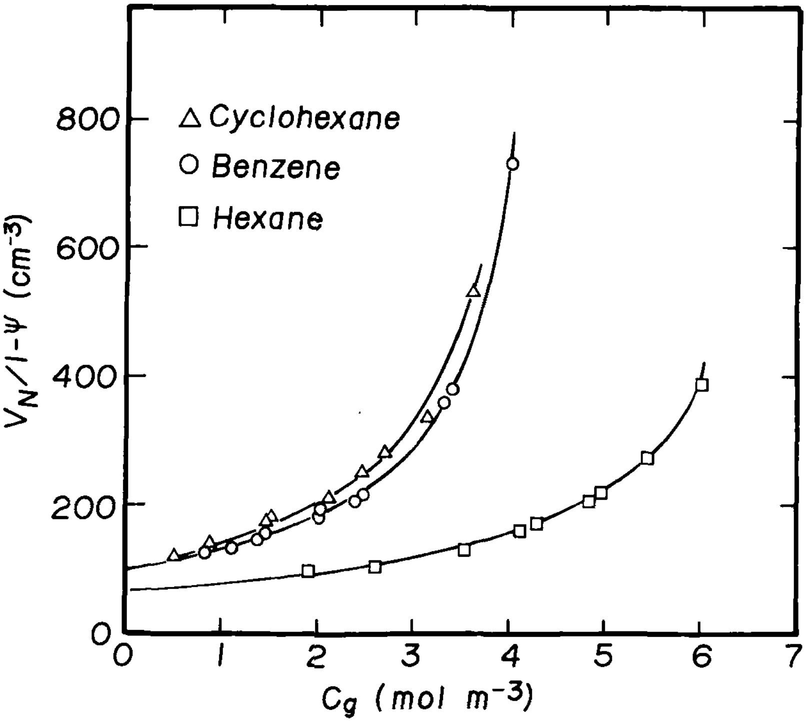

FIG. 2. Plot of $V_N/(1 - \psi)$ versus vapor concentration for PDMS-solvent systems at 25°C.

TABLE 1. Properties of the Pure Components at 25°C

	Saturated vapor pressure, torr	Second virial coefficient, cm^3/mol	Density, g/cm^3	Specific Hard-core volume, cm^3/g
Hexane	150.40	-1.935	0.6549	1.1544
Benzene	94.90	-1.478	0.8738	0.8860
Cyclohexane	97.30	-1.717	0.7738	1.0012
PDMS	-	-	0.9690	0.8399

integral in Eq. (10) is equivalent to finding the area under these curves, this means that small variations in concentration can cause appreciable errors in the values of q and other derived values. Weight fraction activity coefficients obtained from these results are shown in Fig. 3.

Comparison of the GC results with those of other workers could be made in terms of the solvent activities or activity coefficients. However, although these values are useful in, for example, process engineering, the polymer-solvent interaction parameters are of more fundamental interest. Also, these values are more susceptible to variations in experimental conditions, and so provide a better comparison of the different techniques.

Figure 4 shows the interaction parameters for the three systems studied here together with the results of other workers. Chahal, Kao, and Patterson [27] and Flory and Shih [24] studied the PDMS-benzene system at 25°C using a McBain-Bakr type microbalance, and their results are shown as open points in the figure. In this type of apparatus a polymer sample is suspended from a calibrated quartz spiral and exposed to solvent vapor. The weight change as solvent is absorbed is followed by the extension of the spiral, and the solvent pressure is measured by using a mercury or glycerol manometer. However, at low pressures and weight changes, i.e., at low solvent concentrations, results become inaccurate, and this is indicated by the large scatter in the values in Fig. 4. Chahal et al. estimate an accuracy of 0.01 to 0.05 in χ^* depending on the system and the concentration.

In response to the requirement for more accurate results at low concentrations, for example, to compare with infinite-dilution GC results, commercial electronic vacuum microbalances were adapted for use in polymer solution studies. The more sensitive monitoring of weight changes combined with electronic pressure measurement can lead to accuracies of the order of 0.002 to 0.005 in favorable cases, an order of magnitude improvement over the quartz spiral balance. Equipment of this type has been used where accurate results at low concentrations were needed [28] or where small differences between similar samples were being measured [29].

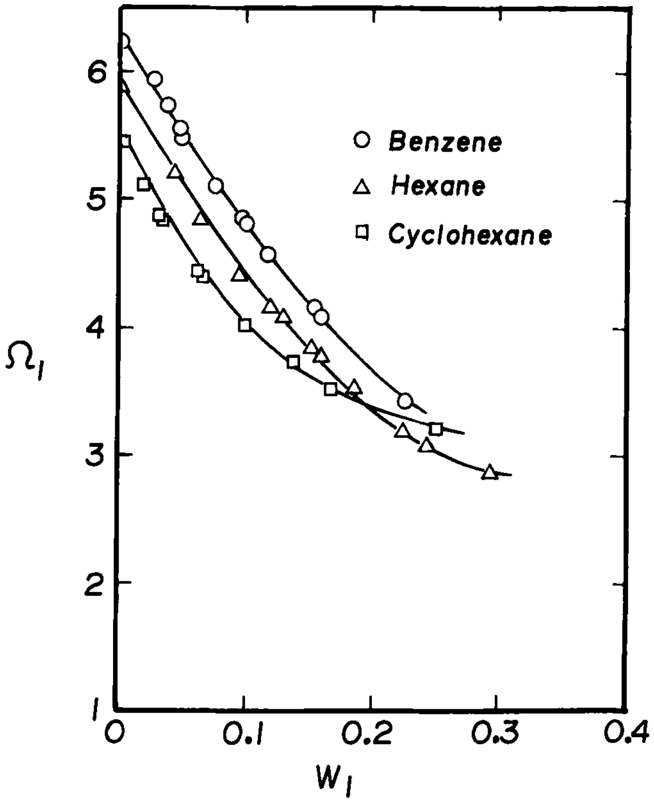

FIG. 3. Weight fraction activity coefficients for PDMS-solvent systems at 25°C.

The major disadvantage with these microbalances is that they cannot be used at high solvent pressures and so are limited to a relatively small concentration range. Recently, a new type of vacuum microbalance in which the balance and polymer sample are in separate chambers and connected by a magnetic coupling has been used for solution studies by Ashworth and Price [30]. This instrument retains the sensitivity of the electronic microbalance but allows a much larger concentration range to be covered. Results for PDMS-solvent systems obtained with this apparatus are shown in Fig. 4 as the solid points.

The results from the present GC study are also shown in Fig. 4 and so may be compared with those from the vapor sorption studies. In each case the values obtained by GC are lower. This is to be expected since the microbalance results were measured on polymers

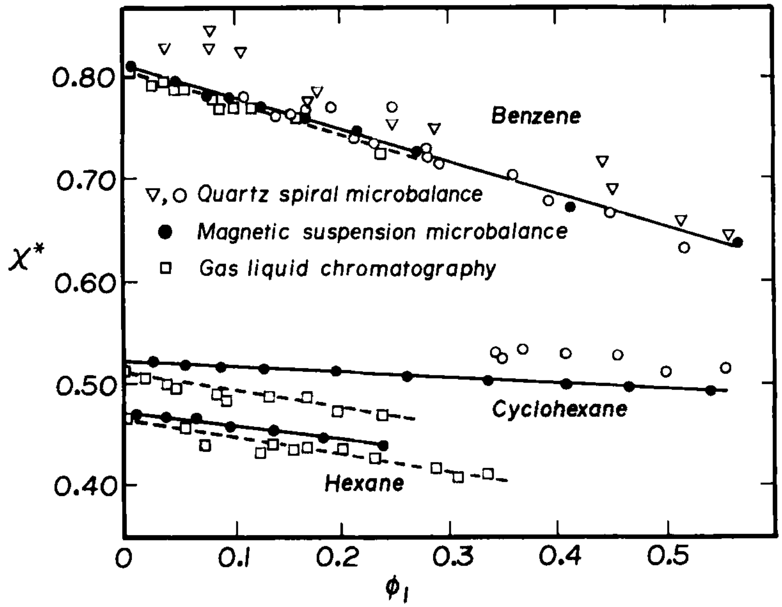

FIG. 4. PDMS-solvent interaction parameters at 25°C.

of considerably higher molecular weight, 89 000 to 500 000, than that used in the current work. A small variation of interaction parameter with molecular weight has been detected for PDMS with benzene and hexane at 30°C [31]. The differences in χ between high molecular weight polymers and those comparable to that used in the current work amounted to 0.005-0.01, which would bring the results in Fig. 4 into exact agreement. A similar variation has also been detected at low polymer loadings, but this is unlikely to be a factor in the present work since a solid support of larger particle size was employed here which would give equivalent film thicknesses at lower loadings.

The agreement between the sets of results for the benzene-PDMS system is excellent if the scatter of the quartz spiral data at low concentrations is ignored. Similarly, good agreement is found with hexane as the solvent (no quartz spiral results are available for this system). Results for the cyclohexane-PDMS system are more divergent. The magnetic suspension microbalance results of Ashworth and Price [29] are considerably lower than the quartz spiral results of Flory and Shih [24], a finding also reported by Brotzman and Eichinger [32]. The GC results are even lower and there is a significant difference in the concentration dependence of χ^*. The reasons for the nonagreement of these results is not clear although, even here, the differences are not excessive.

Comparison of GC with Other Experimental Methods

Another type of vapor sorption apparatus is based on the piezoelectric sorption detector and has been used by Bonner and coworkers [33, 34]. The change in oscillation frequency of a quartz crystal covered with a thin film of polymer is used to detect the weight change as solvent vapor is absorbed. However, no results from PDMS-solvent systems using this method have been published.

A number of factors need to be considered when deciding which technique to employ for a particular study. Perhaps the most important of these is the accuracy of results that may be expected.

Brockmeier et al. estimate the accuracy of their interaction parameters for polyethylene systems at 120°C to be in the region of 5%. From consideration of the precision of retention times, flow rates, etc. in the current work, the accuracy of the present results is estimated to be in the range 2-5%, depending on the system and the concentration involved. From consideration of the scatter of the results in Fig. 4, the GC values are of a similar precision to the quartz spiral results at higher concentrations but are better as infinite dilution is approached. Whereas the vapor sorption results are more accurate at higher concentrations, the reverse is true for GC since larger injection volumes have to be used, which strains the theory on which the calculations are based. Also, at large vapor concentrations the chromatographic peaks become more spread out, making measurement of the retention times less precise. The precision of the electronic vacuum microbalance is superior across the range.

The concentration range open to study by GC is limited ultimately by the requirement that the saturator temperature must be below that of the column. In practice though, the factors set out in the previous paragraph impose further limitations, and the highest usable saturator temperature was about 23.5°C for a column at 25°C. The saturated vapor pressures of benzene and cyclohexane at 25°C are about 95 torr so that, around atmospheric pressure, the mole fraction of solvent in the carrier stream is limited to ~0.12; the limit for hexane is ~0.20 due to the higher P° value of ~150 torr. Clearly, at higher temperatures, higher solvent concentrations may be used, Brockmeier et al. having used vapor mole fractions up to ~0.7 at 120°C. The vapor sorption techniques can, in principle, be used at solvent pressures up to saturation although in practice this is not possible since small temperature fluctuations cause large changes in solvent partial pressures. The solution concentration range possible in the PDMS-cyclohexane system was found to be $\phi_1 \approx 0\text{-}0.6$ [30].

The determination of an absorption isotherm with the piezoelectric sorption method is fairly rapid since a thin polymer film is employed. The GC results reported here were determined over the course of

1-1.5 days. This is comparable to vacuum microbalances with PDMS although with some polymers a period of a week or so may be required for an isotherm, particularly if bulk polymer is used rather than a polymer spread onto a solid support.

Other factors to be considered include the temperature range and the amount of material necessary for the experiment. Although quartz spiral microbalances have occasionally been used at elevated temperatures, the use of vacuum microbalances is usually restricted to temperatures around ambient. This restriction does not apply to the piezoelectric sorption apparatus or to GC where the water bath used in the current apparatus can be replaced by an oil bath or a conventional gas chromatograph oven. The piezoelectric sorption detector is useful in that it may be used with very small (submilligram) amounts of polymer. A quartz spiral microbalance requires about 50-100 mg of polymer for accurate results, whereas the electronic vacuum microbalances and GC apparatus need 0.2-2 g for operation.

CONCLUSIONS

The technique of finite concentration gas chromatography has been used to determine activity coefficients and interaction parameters for solutions of PDMS in benzene, cyclohexane, and hexane that are in very good agreement with results obtained by vapor sorption methods.

Although vapor sorption methods employing electronic vacuum microbalances probably give the most accurate results over the widest composition range around room temperature, GC is a useful technique at low solvent concentrations where quartz spiral microbalances become inaccurate. Also, the GC method, as with the piezoelectric sorption apparatus, is more versatile and allows measurements over a wide range of temperature, etc.

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