USE OF THE MAGNETIC SUSPENSION BALANCE FOR THE STUDY OF POLYMER SOLUTIONS

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ABSTRACT

The method involves the isothermal gravimetric determination of the absorption of an organic vapour into a thin film of liquid polymer spread upon an inert particulate support. Results are presented for the absorption of benzene and cyclohexane at $25^\circ C$ in poly (dimethylsiloxane), and the concentration variation of the interaction parameter determined is compared with that found by other workers.

The determination of the partial molar enthalpy of mixing was also examined by studying the absorption of hexane in poly (dimethylsiloxane) over the temperature range of 25 to $35^\circ C$, and comparing the value obtained with published values.

INTRODUCTION

Previous contributions to conferences on Vacuum Microbalance Techniques have described the use of three types of microbalance to study the thermodynamic properties of liquid mixtures (ref.1, 2, 3). The last of these introduced the use of the Sartorius magnetic suspension balance for this purpose and showed how it combined the attributes of the quartz spring and Sartorius electronic beam microbalances. The method involves the isothermal measurement of the absorption of the vapour of a volatile liquid into a thin film of an involatile liquid spread on an inert particulate solid. Previous studies have used large organic molecules such as squalane or dinonyl phthalate as the involatile liquid. The aim of this work was to extend the technique to the study of polymer solutions. There were two main reasons for the choice of poly (dimethylsiloxane), PDMS, as the polymer for study. Firstly it is one of the few high molecular weight polymers available as a liquid at room temperature, and secondly its thermodynamic properties are well documented in the literature and provide a means of comparing the performance of the balance for this purpose with methods using other apparatus.

One of the interests in polymer solutions lies in the state of "infinite dilution" when the concentration of the volatile component approaches zero. Also of importance is the determination of properties over a wide concentration range, especially for the assessment of modern solution theories. It was thought that the magnetic suspension balance would prove useful in both of these

applications. Since the absorption chamber is completely separated from the balance mechanism, large relative vapour pressures can be used without affecting the balance thus allowing measurements across a wide concentration range, while the good load to precision ratio of the balance gives results accurate enough for reliable extrapolation to infinite dilution (ref.3).

The thermodynamic property calculated directly from the experimental measurements is the activity coefficient of the volatile liquid, which gives a measure of the deviation of the solution from ideal behaviour. However, previous work with the balance has shown that the Flory-Huggins interaction parameter values are more susceptible to variations in experimental measurements and so provide a better indication of the performance of the balance. The variation of the interaction parameter with concentration has been measured for benzene and cyclohexane in PDMS at 25°C and the results compared with those of other workers. The variation of the absorption with temperature can be used to determine the partial molar enthalpy of mixing of the volatile component. This was investigated for n-hexane in PDMS over the range 25 to 35°C and the values obtained compared with published values.

EXPERIMENTAL

Apparatus

The apparatus used has been described previously (see Fig.1, ref.3). The Sartorious model 4201 magnetic suspension balance was used on the intermediate range 1 allowing a weight increase of up to 10 g on a 20 g initial load to be monitored at a resolution of 0.1 mg. The sample of PDMS coated on a diatomaceous earth contained in an aluminium foil bucket was suspended from the lower suspension magnet and enclosed by a glass hangdown tube joined with a rotatable Con-flat joint, using a copper gasket, to the glass envelope enclosing the lower suspension magnet. Another Con-flat joint connected the hang-down tube to the vacuum pumps, the reservoir of volatile liquid and the pressure gauge. All valves in contact with the volatile liquid were Hoke brass bellows valves to avoid interaction of the organic solvents used with tap greases. The pressure gauge was a Texas Instruments quartz Bourdon gauge with a 1000 torr gauge head allowing the equilibrium pressure to be measured with a resolution of 0.01 torr.

Temperature Control

The determination of the absorption of vapours and hence activity coefficients by this method requires accurate knowledge and control of temperature. The temperatures at which the absorption isotherms were measured were controlled by circulating thermostatted water around the hangdown tube enclosing the sample and monitored using mercury-in-glass thermometers. These were calibrated using a National Physical Laboratory calibrated platinum resistance

thermometer in conjunction with a Tinsley type 5840 resistance bridge.

To ensure that the pressure recorded by the gauge was the true pressure of the vapour in equilibrium with the PDMS solution, the air thermostat around the absorption apparatus was maintained at a slightly higher temperature than that of the thermostatted water and the line to the pressure gauge was heated using heating tape. The air thermostat surrounding the balance mechanism (see Fig.1, ref.3) was also maintained at a temperature above that around the absorption apparatus. The actual temperatures in the experimental determinations are given in Table 1. The water temperature was controlled to within $\pm$ 0.01°C and the air temperatures to $\pm$ 0.1°C.

TABLE 1

Thermostat temperatures ($^{\circ}$C)

Nominal	Water Jacket	Apparatus air thermostat	Balance air thermostat
25	24.94	25.2	26.0
30	29.84	30.5	31.0
35	34.93	35.4	35.9

Load drift

It had been noticed previously that variations in room temperature affected the stability of the balance (ref.3), so this was checked at each of the temperatures at which isotherms were recorded. A brass weight was suspended from the balance and all conditions of temperature set as if for an absorption isotherm determination. The absorption chamber was maintained at a pressure of less than 10^{-4} torr and the indicated weight monitored for a two week period. The load drifts found were + 0.16 mg day^{-1} at 25°C, + 0.1 mg day^{-1} at 30°C and -0.09 mg day^{-1} at 35°C. These values are insignificant in relation to the weight changes measured in the experimental observations reported here.

Materials

The n-hexane was a high purity (> 99.7% by glc) sample from Fluka A.G. The cyclohexane and benzene were BDH Ltd research grade samples of purity > 99.9%.

The poly (dimethylsiloxane) was a Dow Corning DC 200 silicone fluid with a viscosity of 12,500 cs. Low molecular weight material was removed by precipitation from ethyl acetate solution with methanol using the procedure of Flory and Crescenzi (ref.4). The resulting number average molecular weight was determined from the intrinsic viscosity of a toluene solution using the relation derived by Barry (ref.5) and found to be 89,000 (ref.6).

The polymer was spread onto a Phase Separations Ltd Celite 545 AW

diatomaceous earth support of 100-120 mesh size using ethyl acetate as the solvent to give a polymer to support weight ratio of 10:90.

RESULTS AND DISCUSSION

For solutions of low molecular weight components the activity coefficient γ_1 of component 1 in solution is classically defined by eqn.1.

$$\gamma_1 = P_1/(P_1^0 x_1) \tag{1}$$

Where P_1 is the equilibrium pressure of component 1 over the solution, P_1^0 is the saturated vapour pressure at the temperature of the solution and x_1 the mole fraction of the component in the solution. However, when a high molecular weight component such as a polymer is involved, the mole fraction becomes an unsuitable basis for describing the concentration, since the large difference in the molecular weights of the components results in a very small mole fraction range corresponding to a wide range of relative pressure. Also, calculation of the mole fraction requires precise knowledge of the polymer molecular weight, which is often difficult to determine accurately. Other concentration bases may be used but in conformity with the work of Flory and his co-workers on polymer solutions (ref.8) the concentration basis used here is the 'segment' or 'hard core volume' fraction ϕ_1 defined by eqn.2.

$$\phi_1 = w_1 v_1^*/(w_1 v_1^* + w_2 v_2^*) \tag{2}$$

Where w_i is the weight of component i in solution and v_i^* its specific segment volume. The specific segment volume may be determined from the thermal expansion coefficient α and density $(1/v)$ using eqn.3.

$$(v/v^*)^{1/3} = 1 + (\alpha T/3)/(1+\alpha T) \tag{3}$$

A segment fraction activity coefficient $^S\gamma_1$ of the volatile component is defined in eqn.4 which also includes corrections for the non-ideal behaviour of the vapour and the compressibility of the liquid.

$$\ln {}^S\gamma_1 = \ln[P_1/(P_1^0 \phi_1)] + [(V_1^0 - B_{11})(P_1^0 - P_1)/RT] + [B_{11}^2(P_1^{0^2} - P_1^2)/2(RT)^2] \tag{4}$$

Before inclusion in eqn.2 the measured uptakes of vapour by the sample are corrected for buoyancy using the method described previously (ref.3). In eqn.4 V_1^0 and B_{11} are the molar volume of the pure liquid absorbate and the second virial coefficient of pure gaseous absorbate respectively. The V_1^0 values were calculated from densities obtained, together with the v^* values, from ref.9 for

PDMS, from ref.10 for benzene and cyclohexane, and from ref.11 for hexane. The P_1^O values were calculated from published Antoine constants (ref.12), while the B_{11} values for the absorbates were extrapolated from an experimental data compilation (ref.13). Absorption isotherms recorded for benzene and cyclohexane are given in Table 2 and for hexane in Table 3 in terms of the weight of absorbate w_1 absorbed at an equilibrium pressure of absorbate P_1, together with the segment fraction activity coefficient calculated.

TABLE 2

Absorption isotherms for PDMS (1.9641 g.) at 302.99 K

Benzene			Cyclohexane		
W_1/mg	P_1/torr	$\ln {}^{S}\gamma_1$	W_1/mg	P_1/torr	$\ln {}^{5}\gamma_1$
15.03	4.52	1.7903	45.08	11.09	1.4629
93.24	24.08	1.6769	97.55	21.94	1.4027
151.17	35.06	1.5978	160.52	32.67	1.3371
201.58	43.06	1.5397	245.65	44.17	1.2581
273.16	52.24	1.4624	394.61	58.45	1.1387
393.60	63.68	1.3491	559.90	70.70	1.0046
517.21	71.40	1.2431	804.16	78.26	0.8994
693.66	78.68	1.1176	1044.1	83.82	0.7996
1312.0	89.12	0.8208	1415.6	88.83	0.6820
2452.9	93.66	0.5516	1957.0	92.44	0.5603

The resulting activity coefficients can be fitted to the Flory-Huggins expression for the activity of the solvent in a polymer solution to generate values of the interaction parameter, χ .

$$\ln({}^{S}\gamma_1\phi_1) = \ln \phi_1 + (1-1/r) \phi_2 + \chi\phi_2^{2} \tag{5}$$

In eqn.5, component 1 is the volatile component and 2 the polymer, segment fractions ϕ_i are defined according to eqn.2 and r is defined as the ratio of the molar hard core segment volumes of the polymer and solvent

$$r = (M_2V_2^{*})/(M_1V_1^{*})$$

where M_i is the molecular weight (ref.8).

Flory and Shih (ref.10) determined χ as a function of ϕ_2 at 25°C for benzene and cyclohexane with a PDMS sample of a viscosity average molecular weight ca. 10^5. Their results and these of the present work are compared in Fig.1. Two absorption isotherms were determined for each absorbate with the magnetic suspension balance. Fig.1 shows that the reproducibility of the results is within 0.004 in χ across the concentration range, which is within the

TABLE 3

Absorption isotherms for hexane in PDMS

298.09 K			302.99 K			308.08 K		
W_1 (mg)	P_1 (torr)	$\ln{}^S\gamma_1$	W_1 (mg)	P_1 (torr)	$\ln{}^S\gamma_1$	W_1 (mg)	P_1 (torr)	$\ln{}^S\gamma_1$
17.41	7.64	1.4505	18.36	9.84	1.4468	17.92	11.77	1.4453
56.96	23.07	1.3964	58.37	28.77	1.3884	57.56	34.91	1.3905
103.44	38.35	1.3373	103.53	47.20	1.3384	105.10	58.36	1.3313
158.47	53.28	1.2734	162.71	66.72	1.2683	160.77	80.90	1.2662
228.43	68.47	1.2001	231.37	84.91	1.1977	233.60	104.62	1.1921
316.69	83.30	1.1109	322.73	103.50	1.1145	322.15	126.73	1.1122
446.54	98.91	1.0183	446.06	121.73	1.0192	452.08	150.26	1.0128

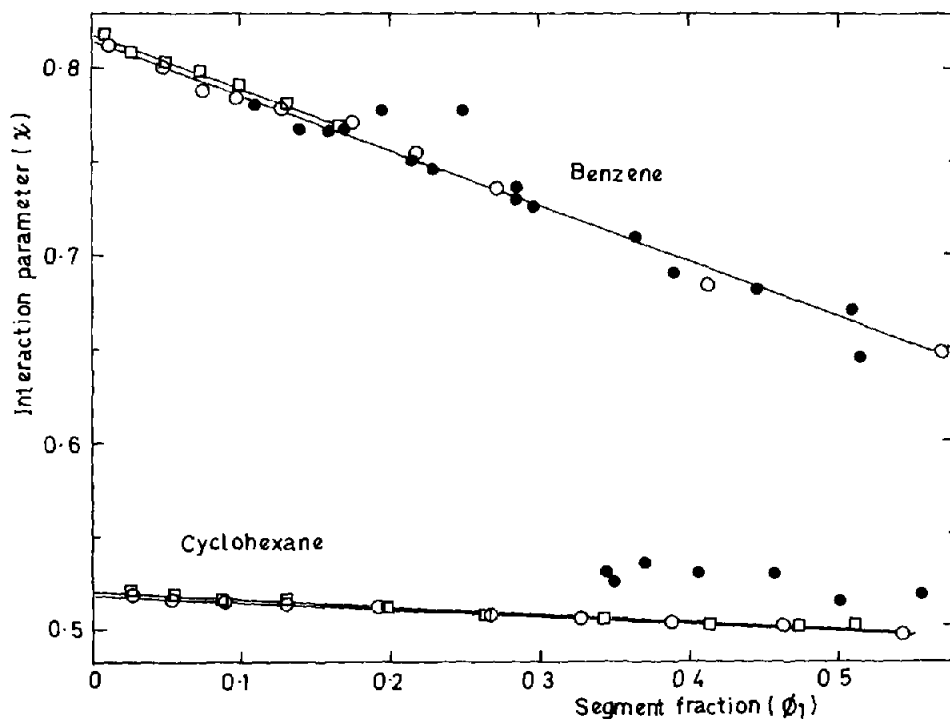(Weight PDMS for 298.09 K = 1.9581 g, for 302.99 and 308.08 K = 1.9642 g)

Fig.1. Variation of interaction parameter with segment fraction for benzene and cyclohexane in PDMS at 25°C. (●) Results of Shih and Flory (Ref.9), (o,□) Results from present work. Full lines show a least squares fit of χ and ϕ_2.

experimental error of the method. The concentration variation of χ was found to be linear as in previous work (ref.3), the fit having a correlation coefficient of ~ 0.99 in each case. The agreement for benzene between this work and that of Flory and Shih can be seen to be excellent. The variation of χ with ϕ and the magnitude of χ are virtually identical in the two studies. The present work shows considerably less scatter in the experimental points, probably because of the greater precision of the magnetic suspension balance compared to that of the quartz spring balance used by Flory and Shih. In the case of cyclohexane the agreement is not as good. There is a similar concentration dependence of χ but the present work gives values about 0.03 lower in χ which is greater than the expected experimental error. The reasons for this are not clear.
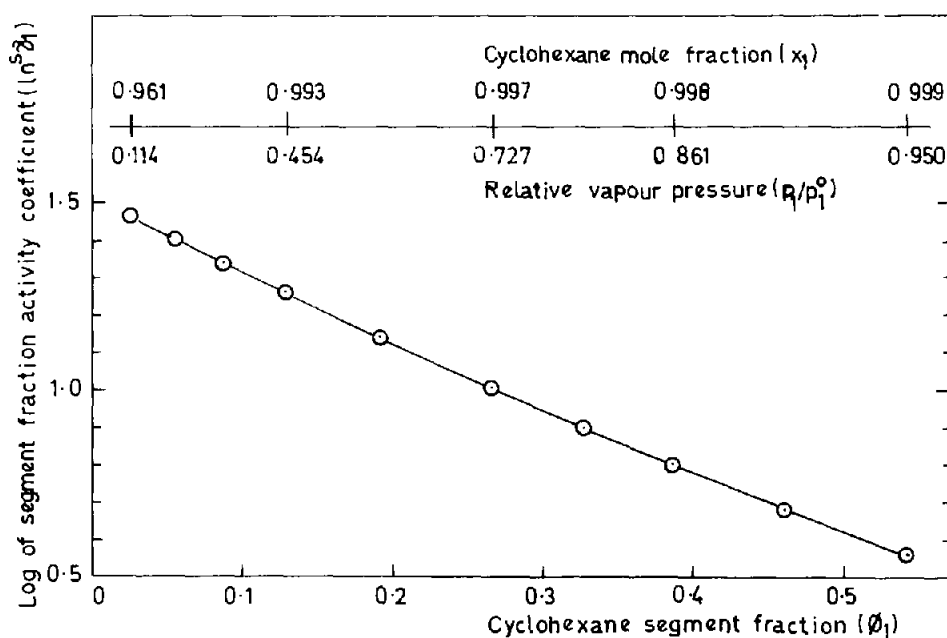

Fig.2. Logarithm of segment fraction activity coefficient for cyclohexane in PDMS at 25°C plotted against cyclohexane segment fraction.

It had been hoped that this balance would allow measurements across the whole concentration range, but it was found that precision decreased above a segment fraction of about 0.6. For example, with the cyclohexane isotherms the point at $\phi_1 = 0.54$ corresponds to a relative pressure of 0.95 and small pressure changes in this region can cause large variations in χ. The point at $\phi_1 = 0.026$

corresponds to a relative pressure of 0.11 but a mole fraction x_1 of 0.96, demonstrating the narrow mole fraction range corresponding to the wide relative pressure range covered, and the unsuitability of mole fraction as a basis for describing polymer solution properties. This is illustrated clearly in Fig.2 which shows the isotherm for cyclohexane in PDMS in terms of the segment volume fraction activity coefficient plotted against the segment fraction and also gives the mole fraction and relative pressure scales.

The activity coefficient calculated from eqn.3 is related to the partial molar free energy of mixing $\Delta \bar{G}_1$ by eqn.6,

$$RT \ln \gamma_1 x_1 = \Delta \bar{G}_1 \tag{6}$$

and the partial molar enthalpy of mixing $\Delta \bar{H}_1$ can be calculated from the temperature variation of the free energy using eqn.7.

$$\Delta \bar{H}_1 = \partial (\Delta \bar{G}_1/RT)/ \partial (1/T)$$
$$= R \partial (\ln \gamma_1)/ \partial (1/T) \tag{7}$$

This relation has been applied to gas-liquid chromatographic determinations of the activity coefficient at infinite dilution γ_1^∞ to obtain the partial molar enthalpy of mixing at infinite dilution $\Delta \bar{H}_1^\infty$. To achieve a comparison with the present work, the determined results were analysed using eqn.8.

$$\chi = \chi^0 + \chi' \phi_2 \tag{8}$$

The interaction parameter at infinite dilution χ^∞ is thus the sum of χ^0 and χ', (ie. $\phi_2 \longrightarrow 1$ as $\phi_1 \rightarrow 0$), and may be used in eqn.5 to calculate γ_1^∞. It has also been shown (ref.7) that $\Delta \bar{H}_1$ can be calculated using eqn.9

$$\Delta \bar{H}_1^\infty = \partial \chi^\infty / \partial (1/T) \tag{9}$$

The isotherms for the absorption of n-hexane in PDMS at 25 and 35°C are shown in Fig.3 as the logarithm of the segment fraction based activity coefficient plotted against the segment fraction. The results at 30°C have been omitted for clarity. The results obtained after extrapolation to infinite dilution are given in Table 4. The partial molar enthalpy of mixing at infinite dilution at a mean temperature of 303.085 K was calculated to be 423 J mol^{-1} assuming:

$$\frac{\Delta \bar{H}_1^\infty}{R} = \frac{\partial (\ln \gamma_1^\infty)}{\partial (1/T)} = \frac{[\ln \gamma_1^\infty (298 \text{ K}) - \ln \gamma_1^\infty (308 \text{ K})]}{[(1/298.09) - (1/308.08)]}$$
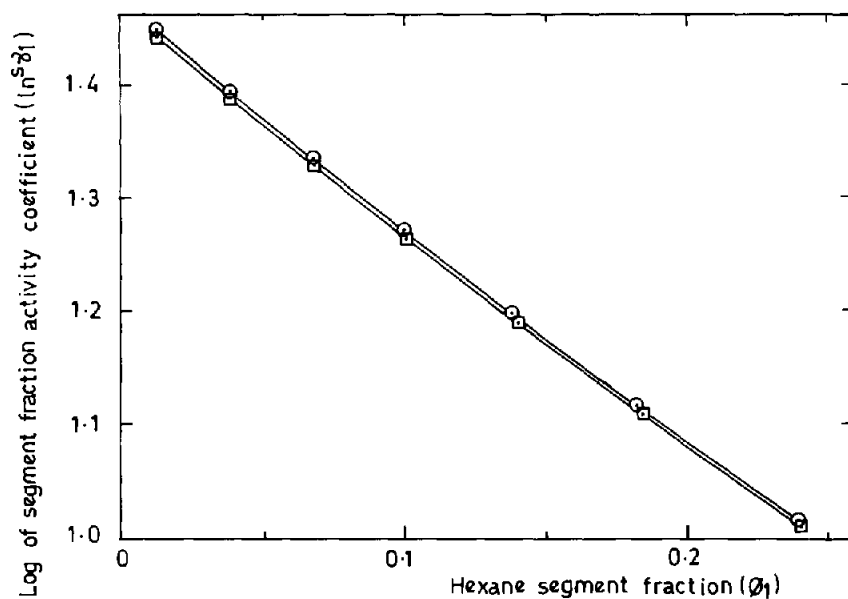
Fig.3. Logarithm of segment fraction activity coefficient for hexane in PDMS at 25°C and 35°C plotted against hexane segment fraction. (⊙) 25°C, (▣) 35°C Full lines show best fit to Flory-Huggins theory (see text).

TABLE 4

Activity coefficients and interaction parameters at infinite dilution of hexane in PDMS

T/K	$\ln{}^S\gamma_1$	χ^∞	sd χ^∞
298.09	1.4752	0.4766	0.0004
302.99	1.4720	0.4734	0.0013
308.08	1.4697	0.4711	0.0006

This assumption is justified by the linear dependence of $\ln{}^S\gamma_1^\infty$ on reciprocal temperature. The value of $\Delta\bar{H}_1^\infty$ determined may be compared with a value of 480 ± 210 J mol^{-1} at 30°C measured on a sample of 30,000 viscosity average molecular weight PDMS by Hammers et al using gas-liquid chromatography (ref.14). Patterson and co-workers derived values of an enthalpic interaction parameter χ_H $(= \Delta\bar{H}_1/RT\ \emptyset_2^2)$ from a calorimetric investigation (ref.15). The value at $\emptyset_2 = 1$, at infinite dilution of the hexane in the PDMS, was approximately 0.18 ± 0.03 at 20°C for PDMS samples of about 20,000 number average molecular weight. This corresponds to a $\Delta\bar{H}_1^\infty$ value of 438 ± 70 J mol^{-1}. In the present

work, the $\ln \gamma^\infty$ and χ^∞ values should be accurate to $\pm$ 0.002 leading to an error in $\Delta \bar{H}_1$ of about 200 J mol^{-1}. The errors inherent in deriving enthalpies by differentiation of free energy data with respect to temperature, as used here and in the commonly used glc measurements, are considerably greater than those involved in direct calorimetric studies. However, the agreement with the glc work is good when the errors are considered, but the value is somewhat lower than the calorimetric result especially when the temperature difference is taken into account.

ACKNOWLEDGEMENTS

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