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USE OF THE MAGNETIC SUSPENSION BALANCE FOR THE STUDY OF LIQUID MIXTURES

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ABSTRACT

Previous contributions to the 9th and 12th V.M.T. Conferences have described the use of microbalances to study the absorption of hydrocarbon vapours by essentially involatile liquid absorbents to determine solution thermodynamic properties. The quartz spring balance is useful over the greater part of the relative vapour pressure range but lacks precision in the lower part of the range as the absorption decreases. In this lower pressure region the greater sensitivity and greater load capacity of the commercial beam vacuum microbalance can be utilised and the measurements extrapolated with confidence to give the activity coefficient for the absorbed vapour at infinite dilution in the liquid absorbent. However, interaction of the volatile hydrocarbons studied with the components of the balance limits the use of the latter balance to the lower pressure region.

The Sartorius magnetic suspension balance combines the attributes of these two balances in that it is not affected by the organic vapours studied and provides the load-to-precision ratio that the determination of accurate activity coefficients requires. This enables liquid mixtures with one volatile and one or more involatile components to be studied over the entire concentration range on the one apparatus. Results are reported for the absorption of hexane by squalane (hexamethyl tetracosane) and compared with those previously determined using a quartz spring balance and a Sartorius electronic microbalance. The modifications found necessary to the magnetic suspension balance for this work are described.

INTRODUCTION

The use of quartz spring and beam vacuum microbalances to determine liquid solution properties has been the subject of two previous contributions to Conferences of Vacuum Microbalance Techniques (ref. 1,2). The method involves the measurement of the isothermal absorption of the vapour of a volatile liquid by an involatile liquid acting as an absorbent on the balance. The involatile liquid is spread upon an inert particulate solid to produce a film of liquid, as in gas-liquid chromatography, in order to reduce the time to reach equilibrium. There are, however, restrictions on speeding up the method using this technique. As the film is made

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thinner, the proportional weight of the solid support becomes greater and the amount of liquid absorbent that can be studied on the balance becomes smaller. Moreover, there is the possibility of introducing an error in the measurement of the solubility from adsorption at the solid and liquid interfaces as the film thickness is reduced.

The greater part of the relative vapour pressure range, that is the vapour pressure of the solution relative to the saturated vapour pressure of the pure liquid absorbate, may be studied with the McBain or quartz spring balance, but the precision with this balance becomes inadequate below a relative vapour pressure of about 0.3 as the absorption of the absorbate decreases (ref. 1). A Sartorius electronic microbalance model 4102 has been used to determine the absorption in the lower pressure range in order that the measurements could be extrapolated with confidence to infinite dilution (ref. 1).

The determination of the activity coefficient of the absorbate at infinite dilution in the liquid absorbent is required for comparison with values derived from gas-liquid chromatographic measurements (ref. 3,4). However the interaction of the volatile hydrocarbons studied with the components of the balance limits the use of this balance to the lower relative vapour pressure region. It was thought that the magnetic suspension balance should combine the attributes of the quartz spring balance in withstanding the hydrocarbon vapours and of the beam balance in providing a greater sensitivity. Thus enabling a liquid mixture comprising one volatile component and one or more involatile components to be studied over the entire concentration range on the one apparatus.

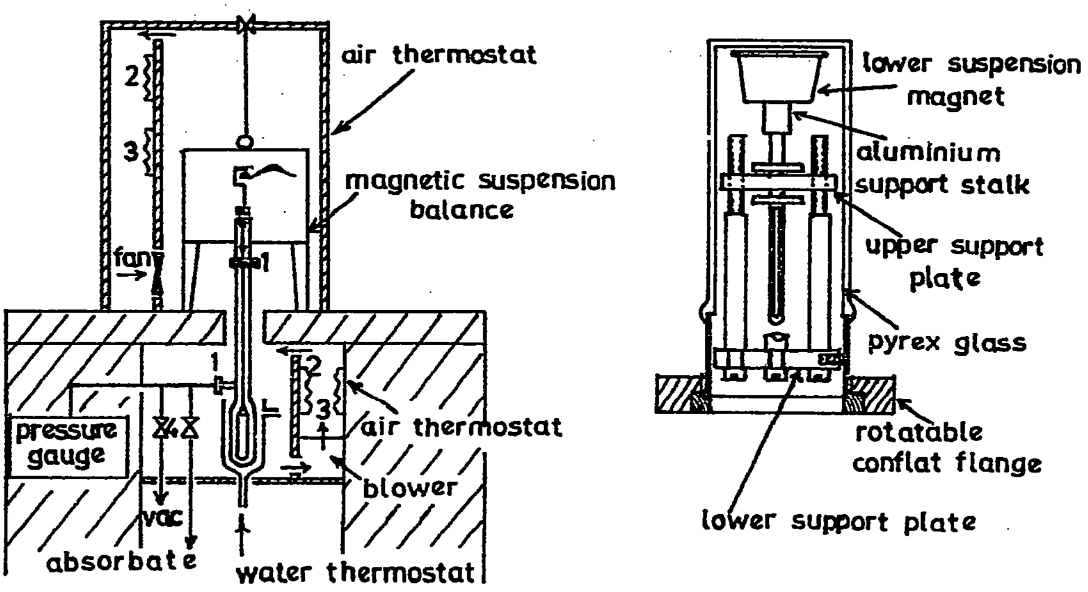
In order to examine the prospective performance of the magnetic suspension balance for this work it is instructive to compare the load-to-precision ratios of the various balances. The quartz springs used in our studies have a total load capacity of about 0.5g and a sensitivity (extension/load) of about 1 mm/mg. With a 200 mg sample containing 20 wt% of liquid absorbent measurements could be made up to a relative vapour pressure of about 0.95 where the absorption is of the order of 5 x amount of liquid absorbent, i.e. 200 mg. A cathetometer reading to 0.01 mm was used to determine the spring extension, giving a precision of about 0.04 mg and hence a load to precision ratio of about 5 x 10^3. The Sartorius electronic balance used for the lower vapour pressure range enabled samples of up to 2g to be studied on the 200 mg measuring range to a precision of 0.02 mg, giving a load-to-precision ratio of 1 x 10^5. The magnetic suspension balance employs a sample weight of 20g and used on the intermediate range with a precision of 0.2 mg gives an identical load-to-precision ratio of 1 x 10^5 but allows the entire relative vapour pressure range to be studied.

The hexane + squalane system was chosen for study since results for this system had been determined previously on the quartz spring (ref. 5) and Sartorius electronic microbalances (ref. 6).

EXPERIMENTAL

Apparatus

A schematic diagram of the apparatus is shown in Fig.1.



apparatus

lower magnet support

Fig. 1. Schematic diagram of apparatus : 1, rotable con-flat coupling; 2, control heater; 3, boost heater; 4, Hoke bellows sealed valves.

The Sartorius magnetic suspension balance enclosed in an air thermostat was supported on a concrete slab mounted on two brick columns. The hangdown tube was also enclosed in an air thermostat and the temperature of the sample, and hence the absorption isotherm, was ensured by circulating thermostatted water at 303.04 ± 0.01 K through a water jacket surrounding the lower part of the hangdown tube containing the sample. The air thermostats and the water thermostat supplying water to the balance housing were controlled at a temperature of 31°C (304 K), just above that of the water jacket around the hangdown tube, to ensure that the pressure measured was the pressure of the vapour in equilibrium with the absorbent sample. The valves in contact with the hexane vapour were Hoke bellows sealed valves. A Texas Instruments quartz Bourdon gauge with a 1000 torr gauge head was used to determine the pressure.

The couplings of the hangdown tube to the glass envelope enclosing the lower suspension magnet and to the vacuum system were made with rotatable Con-flat joints with copper gaskets, and hence were unaffected by the hexane vapour. The support for the lower magnet when not in suspension, shown in Fig. 1, was made of brass to avoid problems of outgassing encountered with the original PTFE support supplied with the balance. This brass support was held in position against the inner wall of the Con-flat joint by three grub screws. The plastic stalk attached to the lower magnet was replaced by an aluminium stalk of equivalent weight to avoid the possibility of the plastic absorbing hexane. The sample bucket was made by folding aluminium foil and was hung from the stalk by alumel wire.

The balance was operated on the intermediate basic range 1 giving a resolution of 0.1 mg on a 20 g load and allowing a possible load increase of 10 g.

Materials

The 2,6,10,15,19,23 - hexamethyl tetracosane (squalane) was a Hopkin and Williams sample material for chromatography. The solid particulate support was J.J.'s (Chromatography) grade M diatomaceous earth chromatography support of sieve sizes B.S.S. 100-200. The squalane was coated on the support by evaporation from a 40-60^{0} petroleum ether solution to give an approximate liquid to support weight ratio of 10:90. The hexane was a high purity sample ($>$99.7% by G.L.C.) from Fluka A.G.

Recorded Load Drift

The measurement of an absorption isotherm throughout the relative vapour pressure range can take a period of several days due to the length of time necessary to reach equilibrium when the equilibrium vapour pressure approaches the saturated vapour pressure. It is therefore important to ensure that the load recorded for a constant weight on the balance does not alter appreciably over such a period.

Early examination with a brass weight on the balance showed considerable variation of the recorded load with time in spite of the thermostatted balance housing. There appeared to be a short term variation dependent on the variation in the daily mean temperature superimposed on longer drift. Eventually the conclusion was reached that as the balance mechanism is open to the atmosphere it is affected by the humidity. The variation in humidity was effectively reduced and the variation of recorded load with time brought within acceptable limits by controlling the room temperature. With the balance thermostatted at 31^{o}C the recorded load remained constant to within ± 0.1 mg day^{-1} over a five day period when the room temperature was controlled at 21 ± 0.6^{o}C with the relative humidity recorded at 38 ± 4%.

Buoyancy Corrections

The corrections for buoyancy are important for this particular work when the measurements are made over the entire relative vapour pressure range. The largest effect is that of the apparent reduction in weight of the sample caused by the increasing vapour density as the relative vapour pressure increases. This can be found by determining the loss in weight of the sample in air (-dw/dp), and the relative loss in weight of a brass weight in the vapour and air giving $\rho vap/\rho air$. The correction to the load for this effect then equals (dw/dp) x ($\rho vap/\rho air$).

A correction must also be made for the effect of buoyancy on the absorbed vapour. This becomes significant as the relative vapour pressure and hence the absorption increases. The correction for the effect of the buoyancy of air on the balance weights is not very significant by comparison with the other two effects.

RESULTS AND DISCUSSION

The absorption measurements for hexane in squalane at 303 K are shown in Table 1 in the form of mole fraction of hexane absorbed x_1 in the squalane at a hexane vapour pressure p_1.

TABLE 1

Absorption of hexane by squalane at 303 K.

x_1	p_1/torr	$\ell n\gamma_1$
0.15104	19.047	-0.37473
0.29331	39.819	-0.30284
0.42501	61.826	-0.23574
0.55367	86.308	-0.16878
0.62092	100.361	-0.13383
0.73589	126.180	-0.07709
0.82710	147.729	-0.03821
0.92732	171.175	-0.00739

The activity coefficient γ_1 of the hexane in the squalane was calculated from these measurements according to eqn.1.

$$\ell n\gamma_1 = \ell n[p_1/(p_1^o x_1)] + (V_1^o - B_{11})(p_1^o - p_1)/RT + [B_{11}^2 (p_1^{o2} - p_1^2)/2(RT)^2] \quad (1)$$

In this equation p_1^o and V_1^o are the vapour pressure and the molar volume, respectively, of the pure liquid hexane, and B_{11} is the second virial coefficient of the pure gaseous hexane. The inclusion of V_1^o corrects for the effect of pressure on the activity of the liquid and B_{11} for the non-ideality of the vapour. The values of p_1^o, V_1^o and B_{11} employed were as previously reported (ref. 5,6).

The logarithm of the activity coefficient is given in Table 1 and the results are compared with those previously determined with the quartz spring balance (ref. 5) and the Sartorius electronic balance (ref. 6) in Fig. 2.

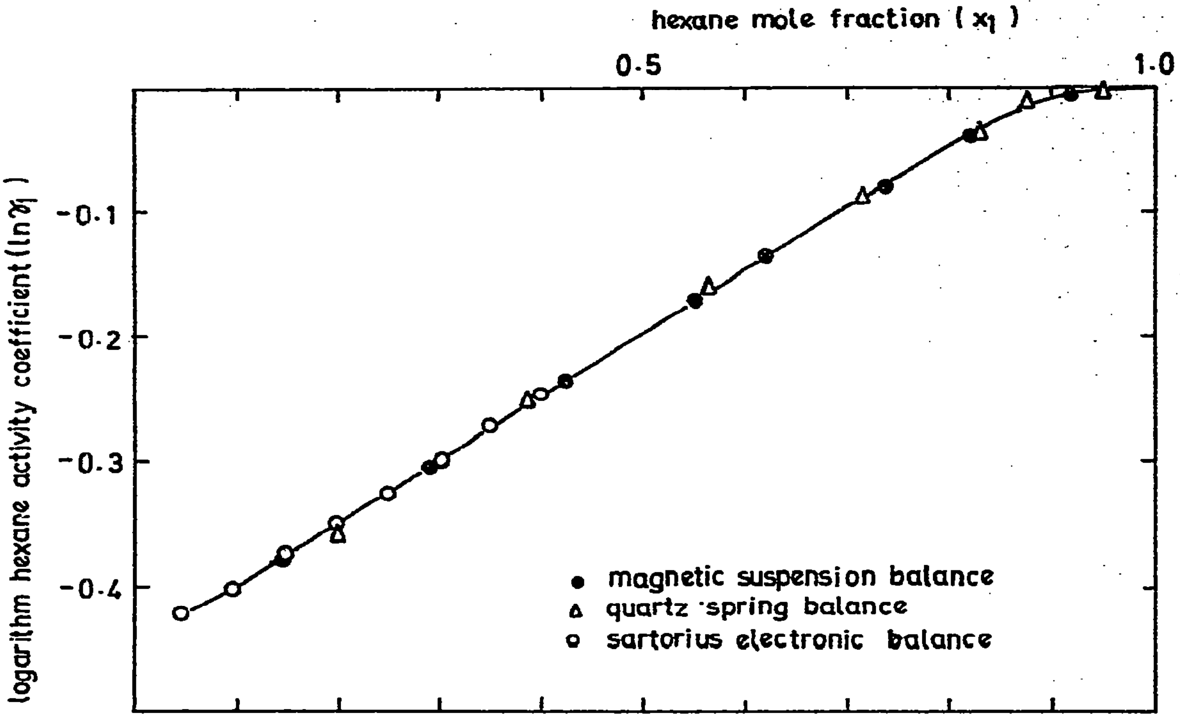


Fig. 2. Logarithm of activity coefficient of hexane in squalane at 303 K plotted against hexane mole fraction.

The result for the lowest absorption determined with the quartz spiral balance can be seen to deviate from the isotherm determined with the other two balances, confirming that the quartz spring balance has inadequate precision for this work below an absorbate mole fraction of about 0.3.

The activity coefficients can be fitted to the Flory-Huggins expression for a binary system (ref. 5), eqn.(2), and the results examined in terms of the parameter χ accounting for the molecular interaction between hexane and squalane.

$$\ln \gamma_1 = \ln (\phi_1/x_1) + 1 - \phi_1/x_1 + (1 - \phi_1)^2 \chi \qquad (2)$$

The volume fraction of the hexane ϕ_1 is defined in terms of the molar volumes of each component according to eqn. (3).

$$\phi_1 = x_1 V_1^o/[x_1 V_1^o + (1 - x_1) V_2^o] \qquad (3)$$

The values of χ determined from the experimental results from the three balances are shown in Fig. 3. The full lines in the figure show the variation of χ as a

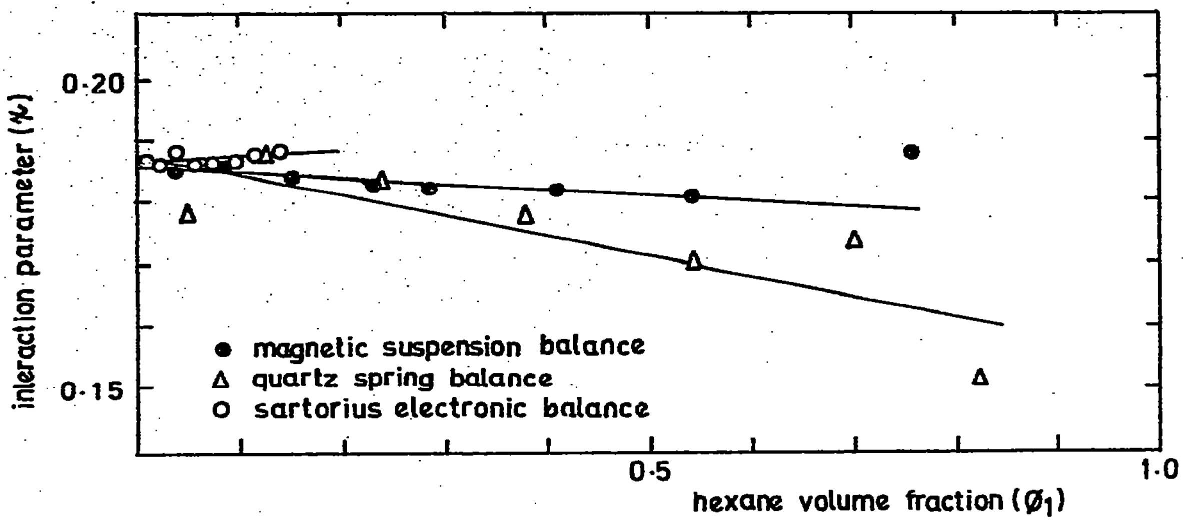


Fig. 3. Interaction parameter for hexane and squalane at 303 K plotted against hexane volume fraction.

linear function of the hexane fraction determined from each set of results. The scatter of the χ values obtained with the quartz spring balance is large compared to those for the other two balances and clearly reflects the lower load-to-precision ratio and the less sensitive method of pressure measurement used. The results for the magnetic balance give a good linear relationship of χ with ϕ_1. The only exception being the experimental point at the highest hexane volume fraction when p_1/p_1^o is about 0.92. Prior to measuring this point the magnetic suspension was lost when switching the mechanical weights, as inadvertently the balance had not been returned to the rest position (factor switch = 0). Thus the zero setting was probably different when the magnetic suspension was regained and the point determined.

The measurements with the Sartorius electronic balance were obtained for the purpose of extrapolation to find the activity coefficient at infinite dilution γ_1^∞ and were limited to the hexane mole fraction range of 0.05 to 0.4. (ref. 6). These results, therefore, only cover a very small part of the volume fraction range. However, the agreement in this range with the results for the magnetic balance is good and the activity coefficient at infinite dilution resulting from extrapolation of the magnetic balance results of 0.6397 agrees well with that of 0.6395 obtained from the Sartorius electronic balance results.

CONCLUSION

The magnetic suspension balance has been found to be very suitable for the measurement of the absorption of hydrocarbon vapours by involatile liquids. It combines the attribute of the quartz spring balance in that its performance is not affected by the organic vapours studied and the attribute of the commercial beam balance in providing a high load-to-precision ratio. This enables the activity coefficients of the volatile component in the liquid mixture to be determined with good precision over the entire concentration range on the one apparatus.

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