

and their mean value for the given temperature is calculated [$h'_{\text{mean}} = (h'_1 + h'_2)/2$]. The thermostat is then re-set, and h'_{mean} is measured at some other temperatures.

The pycnometer is then removed from the thermostat, washed, cut open, emptied, carefully dried, and re-washed. The mass of the calibrating liquid present in the pycnometer is found from the weight difference. Knowing the density of the calibrating liquid, the volumes corresponding to the measured heights can be calculated. Hence we can write the first pycnometric equation in the form

$$V' = a' + b'h'_{\text{mean}} + c'(h'_{\text{mean}})^2, \quad (1)$$

where the constants a' , b' , and c' are calculated by least squares.

Using exactly the same procedure, the pycnometer is calibrated a second time with enough liquid to reach to the mark 5. The distances h''_1 and h''_2 for the liquid menisci in tubes 4 and 10 are measured, and the mean values $h''_{\text{mean}} = (h''_1 + h''_2)/2$ are calculated for the chosen calibration temperatures. From these results we obtain the second pycnometric equation

$$V'' = a'' + b''h''_{\text{mean}} + c''(h''_{\text{mean}})^2. \quad (2)$$

After calibration, the apparatus is washed and dried, and used to measure the density of two liquids with limited mutual solubility. The heavier liquid is added through tube 2, followed by the lighter liquid, in amounts such that the interface is in tube 7 and the meniscus of the lighter liquid is above mark 5. Tube 2 is again sealed off, the apparatus is clamped in a rotary shaker, and placed in the thermostat.

When the apparatus has reached the desired temperature, it is rotated round an axis perpendicular to the plane of the paper through 180° anticlockwise, and then returned to the vertical position, using a hydraulic device or a servo-motor. This motion causes mixing of the liquids in the mixing reservoir 1, and no liquid enters tube 2. Mixing is continued for several hours at the chosen temperature until mutually saturated solutions are obtained. The pycnometer is returned to the vertical position, and the liquids are allowed to settle until interfacial boundaries appear in tubes 7 and 10. The pycnometer is rotated round an axis perpendicular to the plane of the paper, and some of the lighter liquid is poured out of tube 10 so as to bring the interface to the middle section of tube 7. The apparatus is allowed to reach thermostat temperature for several hours, until the positions of the menisci have become stable, and the density measurement is begun. The distances from the mark 3 to the menisci of the lighter (h_{11} and h_{12}) and the heavier (h_{21} and h_{22}) liquid in tubes 4, 7, and 10 are noted.

Using the calibrating equations (1) and (2), the volume V_1 of the heavier liquid is determined by inserting into Eqn. (1) the value $h_{1\text{mean}} = (h_{11} + h_{12})/2$, and the total volume V by inserting into Eqn. (2) the value $h_{1\text{mean}} = (h_{11} + h_{12})/2$. The volume of V_1 of the lighter liquid is obtained by difference. We can write the two equations

$$V_1\rho_1 + V_2\rho_2 = m, \quad (3)$$

$$(h_{22} - h_{12})\rho_1 = \Delta h_{21}\rho_2 + (h_{21} - h_{11})\rho_1. \quad (4)$$

where m is the combined mass of the two liquids, Δh_{21} is the difference between the levels of the solution of the heavier liquid in the heavier liquid in tubes 7 and 10, ρ_1 and ρ_2 are the densities of the saturated solutions of the heavier in the lighter liquid and vice-versa.

Inserting values of V_1 , V_2 , m , h_{12} , h_{11} , h_{22} , h_{21} , and Δh_{21} in Eqns. (3) and (4), the densities ρ_1 and ρ_2 are determined by solving the equations simultaneously. An important feature of the present pycnometer is the fact that the masses of the individual liquid phases (which vary with temperature because of solubility differences) do not need to be separately known. The total mass, however, remains constant irrespective of temperature, and is readily determined by weighing at the end of the experiment.

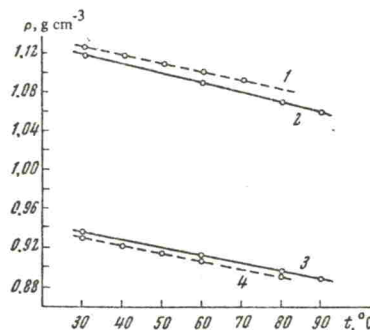


Figure 2. Density polytherms for the PEG-DBS system: 1) for pure PEG; 2) for a saturated solution of DBS in PEG; 3) for a saturated solution of PEG in DBS; 4) for pure DBS

The pycnometer has been used in our laboratory to measure the density of a number of systems. In particular, the following polytherm equations have been obtained for the density in the poly(ethylene glycol)-dibutyl sebacate (PEG-DBS) system (see Fig. 2):

$$\rho_{\text{DBS}} = 0.9504 - 0.0005619t + 0.000001731t^2, \quad (5)$$

$$\rho_{\text{PEG}} = 1.14704 - 0.0011236t + 0.000001485t^2. \quad (6)$$

The mean scatter of the experimentally measured densities from these curves is less than 0.0001 g cm^{-3} .

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Mass-spectrometric Assembly for Studying the Solubility of Gases and Gas Mixtures in Liquids at High Pressures

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A fast mass-spectrometric procedure for measuring the solubility of gases and gas mixtures in volatile liquids at different temperatures and at pressures between 1 and 150 atm has been developed. The mass spectrometer has a capillary sample injection system which allows the composition of the liquid in the high-pressure vessel to be determined by continuously sampling the liquid at a rate of $\sim 10^{-8} \text{ g s}^{-1}$. Plots of the solubility of argon in benzene and in toluene as a function of pressure at 20 ± 1 and $17.3 \pm 0.2^\circ \text{C}$ are given.

Several methods of measuring the solubility of gases in liquids are known^{1,2}, but they all suffer from serious shortcomings. The most widely used is the manometric