

A DILUTION DILATOMER FOR MEASURING EXCESS VOLUMES

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A dilatometer is described which, as to its conception, stems from the dilatometer used by Kumaran and McGlashan (1977). The dilatometer was employed for measuring excess volume of the benzene-cyclohexane mixture at a temperature of 25°C. The measured data agree well with those reported in the literature.

A number of dilution dilatometers for measuring excess volumes, based on the principle which has been described first by Geffcken and coworkers¹, is published in the literature. Those dilatometers, however, have a greased stopcock which is one of often discussed sources of errors. Bottomley and Scott² have described a tilting dilution dilatometer without any stopcock which is to be handle during measurement. This dilatometer, however, suffers from several drawbacks: it is difficult to calibrate, the dilatometer filling is carried out under vacuum and the liquids to be mixed are separated only by a capillary and consequently it is not possible to exclude the effect of diffusion. Kumaran and McGlashan³ have described an improved version of the dilatometer by Bottomley and Scott² which does not have the above-mentioned disadvantages.

In this work a dilution dilatometer is described which in its basic arrangement issues from the Kumaran and McGlashan³ design. This dilatometer has been used for measuring excess volume of the benzene-cyclohexane mixture at a temperature of 25°C and its function has been checked by comparing the measured data with the literature ones.

EXPERIMENTAL

Dilatometer

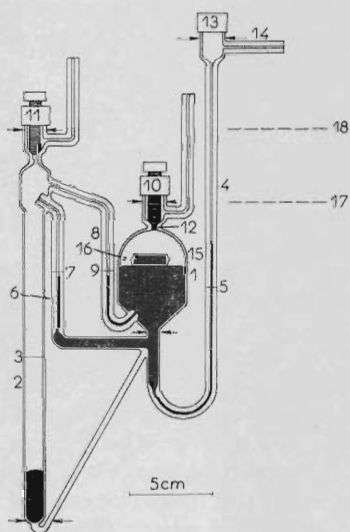
The dilatometer is shown in Fig. 1. It differs from the original version by Kumaran and McGlashan³ so that the lower part of the burette 2 is not blown into a spherical bulb which in the original version serves for determining the amount of component present in the mixing bulb 1 at the beginning of measurements. Further difference consists in the detail that the capillary 6 is led outside the burette and leads into it as far as at its upper part. This arrangement makes it possible to utilize

better the component transferred from the burette into the mixing bulb and, in addition, to make the vertical dilatometer size smaller and to increase the utilizable length of burette. To measure all the concentration dependence of excess volume of a binary mixture in two runs it is required less than 50 cm^3 of each component.

The mixing bulb 1 had a hemispherical part of capacity about 16 cm^3 , the volume of its cylindrical part was about 30 cm^3 . The burette 2 was made of $0.9641 \pm 0.0014 \text{ cm}^2$ cross-section precision-bore tubing, the working burette length was 16 cm. The burette cross section in dependence on the position with respect to the reference mark 3 was determined by repeated calibration with mercury. The burette cross section was then read from a calibration curve in every measurement of excess volumes. The cross section of the capillaries (precision-bore tubing) was determined by calibration with mercury, *i.e.* by measuring the column length of mercury of known mass inside the capillary. The cross section of capillaries 6 and 8 was found to be $(7.8984 \pm 0.0014) \cdot 10^{-3} \text{ cm}^2$ and $(7.8775 \pm 0.0065) \cdot 10^{-3} \text{ cm}^2$. For the measuring capillary 4 (mean cross section $4.95 \cdot 10^{-3} \text{ cm}^2$) the dependence of the capillary cross section on the meniscus position with respect to the reference mark 5 was determined by calibrating. During measurements the capillary cross section was then read from calibration curve. On calibrating the capillary 4, the correction for the meniscus curvature of the mercury cylindrical column was taken. It was assumed that the meniscus has a shape of spherical cap whose height was always measured by a cathetometer. The valves 10 and 11 were metal-core Teflon needle valves of closed bore 2 mm. The valve cone 10 was lengthened by the Teflon rod 12 which, in case of the closed valve, filled up the space which was inaccessible and hard to stir. The tube 14 serves for connecting the apparatus for determination of corrections for compressibility³ (mercury U-tube manometer and pressure supply).

The dilatometer was fastened to a perspex plate. The plate with the dilatometer was mounted in rotating way on a frame and all the apparatus was placed in a water thermostat bath of volume 40 dm^3 . The frame made it possible to locate the dilatometer in two levels so that the water

FIG. 1
Dilatometer. 1 Mixing bulb, 2 burette, 3 reference mark of burette, 4 measuring capillary, 5 reference mark of measuring capillary, 6, 8 capillaries, 7, 9 reference marks, 10, 11 valves, 12 Teflon extension of valve cone, 13 stopper, 14 tube for connecting the apparatus for compressibility determination, 15 stirrer, 16 point of rotation, 17 thermostat bath level during filling dilatometer, 18 thermostat bath level during measurement. Points of fastening the dilatometer to the plate are designated by arrows (see text)



surface with respect to dilatometer was in the position 17 or 18. The thermostat temperature was controlled with an accuracy of ± 0.003 K by a proportional temperature controller and monitored by means of a platinum resistance thermometer (500Ω) connected in a Wheatstone bridge. The thermostat box was made of plane parallel glass plates. All readings of the mercury meniscus heights in the dilatometer were carried out by use of the cathetometer which allowed to read to 0.025 mm.

Loading and Measurement

Before each measurement the dilatometer was always thoroughly cleaned (with diluted nitric acid, water, ethanol and acetone) and dried. Then it was placed into the thermostat so that the water surface in the thermostat was at the level 17 (Fig. 1). The mixing bulb was filled fully with mercury. The first component was then injected by use of a hypodermic syringe into the burette 2 so that its level was above the level of the inlet of capillary 8 into the burette. Some air remained in the capillaries 6 and 8 and therefore a vacuum pump was connected to the valve 11. Mercury from the mixing bulb then run over through the capillaries 6 and 8 into the burette 2 and so air was removed from the capillaries. As soon as mercury in the burette reached the calibrated part, the vacuum pump was disconnected. Then the component in the burette was filled up until its level got into the valve body 11 and the valve cone was screwed in (the valve, however, was not closed). Mercury in the mixing bulb was filled up so that the stirrer 15 was immersed in mercury. At the places where the stirrer ends touched the mixing cell wall, air bubbles remained which could be removed by submerging the stirrer by means of a thin rod going through the valve 10. Then the mixing bulb was filled up with mercury until its level reached about 1 mm under the seat of valve 10. The cone of valve 10 was screwed home into the valve body and the valve was closed. After thermal equilibration the heights of mercury menisci in the capillaries 4, 6 and 8 were read with respect to the reference marks 5, 7 and 9. The cone of valve 10 was screwed off and by means of a hypodermic syringe, mercury was taken off from the mixing bulb so that its level sank approximately to the beginning of the cylindrical part of the mixing bulb. The withdrawn mercury was weighed with an accuracy of ± 0.1 mg. The second component was then brought into the mixing bulb until its level rose up to the internal space of valve 10. The cone of valve 10 was screwed in and after thermal re-equilibration, the valve 10 was closed. The heights of mercury menisci in the capillaries 4, 6 and 8 with respect to the corresponding reference marks were read again. The number of mol of the component in the mixing bulb was calculated from the mass of withdrawn mercury and from the changes of mercury menisci in capillaries 4, 6 and 8.

Then the vertical position of the dilatometer was so changed that the water surface in the thermostat was at the level 18. After thermal equilibration the valve 11 was closed. Afterwards the stopper 13 was screwed off and by use of a hypodermic syringe with thin polyethylene capillary, mercury was taken off from the capillary 4 so that its meniscus was about 4 cm under the reference mark 5 (for excess volume of the benzene+cyclohexane mixture is positive) and the stopper 13 was again screwed home. After thorough thermal equilibration, the heights of mercury menisci in the capillaries 4, 6, 8, in the burette 2 (with respect to the respective reference marks) and in the mixing bulb were read. The dilatometer was tilted by anticlockwise rotation as far as mercury began to overflow through the capillary 6 into the burette 2 while the component flowed from the burette 2 into the mixing bulb through the capillary 8. After restoring the dilatometer into its initial position, mercury levels in the capillaries 6 and 8 re-established themselves approximately in the position as it is shown in Fig. 1. The content of mixing bulb 1 was thoroughly mixed by rocking the dilatometer and by means of a rotating magnet. After thermal equilibration the heights of mercury menisci in the capillaries 4, 6 and 8, in the mixing bulb 1 and in the burette 2 were read again. The number of mol of the component added from the burette into the

mixing bulb was calculated from the height change of the mercury meniscus in the burette 2 and in the capillaries 6 and 8. The volume change accompanying the dilution was determined from the height change of the mercury meniscus in the capillary 4. Then the height of the mercury meniscus in the capillary 4 was re-adjusted into the position about 4 cm under the reference mark 5 and so the dilatometer was prepared for next measurement. During one run the excess volume for 6–8 concentrations was always measured.

Before starting the measurements and always after each mixing, the compressibility of the dilatometer content was determined by means of the mercury U-tube manometer and the pressure source (about 17 kPa) by measuring the change in the mercury level in the capillary 4 caused by a known overpressure applied to mercury in the capillary 4. The heights of the mercury menisci in the capillary 4 before and after mixing were then corrected for the zero difference of the mercury heights in the capillary 4 and in the mixing bulb 1.

Owing to the temperature instability in the thermostat bath, the mercury meniscus in the capillary 4 exhibited slight oscillations. To eliminate as much as possible the effect of the temperature fluctuations the minimum and the maximum meniscus height was always measured and the average of these values was calculated.

Substances Used

Mercury was washed with diluted nitric acid, water, sodium carbonate solution and again with water. Then it was dried by manifold filtration through a pricked filter paper and distilled under vacuum. Its density at 25°C was 13.5340 g cm⁻³ (ref.⁴).

TABLE I

Excess volume v^E (cm³ mol⁻¹) of the benzene(1)–cyclohexane(2) mixture at 25°C

x_1	v^E	x_1	v^E	x_1	v^E
0.06390	0.1608	0.48388	0.6486	0.63630	0.5958
0.09425	0.2296	0.48829	0.6477	0.64583	0.5856
0.12764	0.2995	0.50749	0.6492	0.68129	0.5569
0.17106	0.3788	0.51114	0.6476	0.72575	0.5088
0.17375	0.3830	0.52690	0.6441	0.73295	0.4991
0.23277	0.4749	0.53063	0.6437	0.74542	0.4839
0.25856	0.5090	0.53570	0.6436	0.77155	0.4496
0.27785	0.5298	0.55275	0.6378	0.80929	0.3929
0.30153	0.5563	0.55462	0.6391	0.82531	0.3676
0.33477	0.5863	0.56916	0.6324	0.83822	0.3431
0.38908	0.6226	0.58450	0.6255	0.86645	0.2940
0.40027	0.6274	0.59118	0.6241	0.91118	0.2035
0.42959	0.6394	0.59916	0.6181	0.93109	0.1606
0.43580	0.6416	0.61217	0.6105	0.94671	0.1267
0.47949	0.6486	0.61245	0.6103	0.95408	0.1087

Benzene and cyclohexane were purified by the procedure described previously⁵. Their densities measured at 25°C by the Ostwald–Sprenzel pycnometer were as follows: benzene: 0.87360 g cm⁻³ (lit. 0.87345–0.87387); cyclohexane: 0.77397 g cm⁻³ (lit. 0.77358–0.77401). Before measuring the densities and always before filling the dilatometer, both components were partly degassed.

RESULTS

To check the dilatometer rigidity and the tightness of the valves 10 and 11, a blank measurement was carried out. Benzene was introduced both into the mixing bulb and into the burette and all the run including the measurement for determination of the compressibility was made. During this blank test no changes in the height of the mercury meniscus in the capillary 4 were observed except slight oscillations due to the temperature fluctuations.

Excess volume of the benzene–cyclohexane mixture was measured in six independent runs. The results are given in Table I. The measured dependence of the excess volume on composition (mole fraction) was fitted to the equation

$$v^E = x_1x_2[2.59432 + 0.10198(x_2 - x_1) + 0.02509(x_2 - x_1)^2] \quad (I)$$

(v^E in cm³ mol⁻¹, the subscript 1 denotes benzene) with a standard deviation equal 0.0009 cm³ mol⁻¹ and a maximum deviation -0.0018 cm³ mol⁻¹. The deviations of individual measured values from those of Eq. (I) are represented in Fig. 2 where the single runs are distinguished as well.

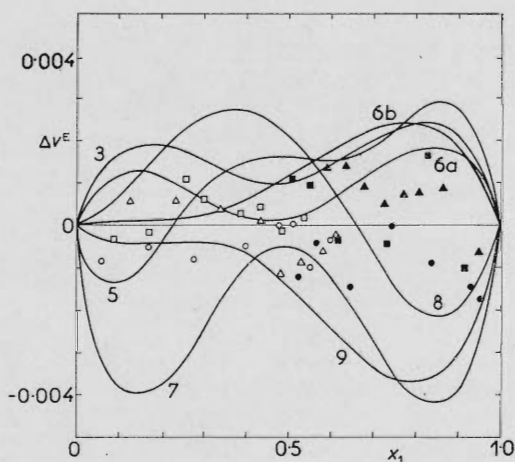


FIG. 2

Deviations of measured values and of some literature data from Eq. (I) in cm³ mol⁻¹. Points represent deviations of the measured individual runs; lines represent deviations of the literature correlated data from Eq. (I). 3 Kumaran, McGlashan³; 5 Cibulka, Hynek, Holub, Pick⁵; 6a Stokes, Levien, Marsh (piston dilatometer)⁶; 6b Stokes, Levien, Marsh⁶; 7 Kowalski, Boniecka, Orszagh⁷; 8 Stookey, Sallak, Smith⁸; 9 Palta, Lark⁹

TABLE II

Comparison of measured and literature values of excess volume of the benzene(1)–cyclohexane(2) mixture at 25°C

$\Delta \cdot 10^3$ ^a cm ³ mol ⁻¹	Sign ^b	Method	Std. dev. of lit. data $\sigma(v^E) \cdot 10^3$ cm ³ mol ⁻¹	Author (ref.)
1.1	+	piston dilatometer	1.4	Stokes (6)
1.4	+	dilatometer	0.8	Stokes (6)
1.6	+	dilatometer	0.7	Kumaran (3)
1.7	+—	vibrating densimeter	1.7	Cibulka (5)
1.8	+—	dilatometer	4.0	Stookey (8)
2.1	—	dilatometer	1.3	Palta (9)
2.8	—	dilatometer	2.9	Kowalski (7)
2.9	+—	pycnometer	4.8 ^d	Oba (25)
2.9	+	vibrating densimeter	1.7	Kiyohara (28)
3.0	—+	dilatometer	2.0	Dickinson (29)
3.0	+	^c	1.6	Handa (30)
3.3	+—	pycnometer	2.0	Kimura (31)
3.4	+—	dilatometer	0.5 ^d	Wood (13)
3.4	+	vibrating densimeter	0.4	Goates (12)
3.5	+—	vibrating densimeter	1.4 ^d	Meyer (32)
3.5	—+	dilatometer	1.6	Brennan (11)
3.8	+—	dilatometer	6.0	Gracia (21)
4.1	—+	dilatometer	3.0	Jain (33)
4.3	+	dilatometer	0.4	Tanaka (14)
4.3	+	magnetic float	1.5	Weeks (15)
4.4	—	dilatometer	5.5	Beath (26)
4.4	+—	vibrating densimeter	4.0	Grolier (34)
4.5	—+	vibrating densimeter	1.9	Radojkovic (16)
4.6	—	dilatometer	3.0	Dixon (22)
4.8	—+	dilatometer	1.3 ^d	Diaz Pena (17)
5.0	—+	pycnometer	8.0	Woycicki (27)
5.3	+	vibrating densimeter	1.3	Goates (18)
5.8	+—	dilatometer	5.0	Letcher (23)
7.5	—	dilatometer	0.5	Powell (19)
8.1	—	dilatometer	7.0	Watson (24)
9.7	—	dilatometer	0.8	Chareyron (10)
9.8	—	piston dilatometer	0.03 ^e	Janssens (20)

^a $\Delta = [\int_1^0 (v_{lit}^E - v_{exp}^E)^2 dx_1]^{1/2}$, where v_{lit}^E and v_{exp}^E are values calculated from the respective correlation relations (*i.e.* from the relation reported by authors and from Eq. (1)); ^b sign of the difference $v_{lit}^E - v_{exp}^E$; the sign given as first is the sign of the integral $\int_1^0 (v_{lit}^E - v_{exp}^E) dx_1$; ^c v_{lit}^E from the equation given by Handa and Benson³⁰ for a set formed by the data^{3,6,14}; ^d our correlation of literature data by a relation of the Redlich–Kister type; ^e in the paper²⁰ given as “average absolute error”.

DISCUSSION

One of the criteria of correctness of the excess volume measurements by dilution dilatometers is overlapping of single runs starting from the opposite ends of the concentration range. It is evident from Fig. 2 that our results of measurement fulfil this criterion for the overlapping is less than $\pm 0.0015 \text{ cm}^3 \text{ mol}^{-1}$.

Comparison of our measured data with the published literature ones is given in Table II; the courses of deviations of some chosen measurements from our measured data are compared in Fig. 2. Very good agreement has been reached with the data obtained by use of different techniques, *i.e.* a dilution dilatometer with greased stopcock⁶, a dilution dilatometer of the same type (*i.e.* without greased stopcock)³, batch dilatometers^{7,8} (in case of the mentioned measurements^{3,6-8} the corrections for the compressibility were carried out in the same way as in this work), a batch dilatometer⁹ and a piston dilatometer⁶, for which the correction for compressibility can be neglected because in the measuring capillary the column of measured mixture and not mercury is observed, and finally, an indirect method when the excess volume was calculated from the mixture densities measured by a vibrating-tube densimeter⁵. When comparing the data, we took into account also the accuracy of the data of this work and of the literature ones (*i.e.* $\sigma(v_{\text{exp}}^{\text{E}}) = 0.0009 \text{ cm}^3 \text{ mol}^{-1}$ and $\sigma(v_{\text{lit}}^{\text{E}})$ according to Table II). The areas delimited by the intervals $v_{\text{exp}}^{\text{E}} \pm \pm 2\sigma(v_{\text{exp}}^{\text{E}})$ and $v_{\text{lit}}^{\text{E}} \pm 2\sigma(v_{\text{lit}}^{\text{E}})$, where $v_{\text{exp}}^{\text{E}}$ and $v_{\text{lit}}^{\text{E}}$ are the values calculated from the respective smoothing equations, were found to have a non-zero intersection in the entire concentration range in case of all data sets except¹⁰⁻²⁰. In case of some less accurate data, Eq. (I) runs in the entire concentration range inside the area delimited by the values $v_{\text{lit}}^{\text{E}} \pm 2\sigma(v_{\text{lit}}^{\text{E}})$ (data sets^{5,6,7,21-24}) or by the values $v_{\text{lit}}^{\text{E}} \pm \sigma(v_{\text{lit}}^{\text{E}})$ (data sets^{8,25-27}).

The deviations of some sets of the literature data^{10,19,20} from the majority of the other data are considerable. Powell and Swinton¹⁹ do not mention in their work any correction for compressibility, which might explain the large negative deviations of their data. In case of the data by Chareyron and Clechet¹⁰, an explanation is difficult for the authors used a dilution dilatometer operating at constant pressure; similarly it is with the data²⁰ when a metallic piston dilatometer of unconventional design was used.

Thus, from the checking of the described dilatometer it is evident that it is convenient for measuring excess volumes of liquid mixtures. The accuracy of the excess volume values is better than $\pm 0.002 \text{ cm}^3 \text{ mol}^{-1}$. To measure all the concentration dependence of excess volume of a binary mixture it is necessary to have comparatively small amount of measured substances which for two runs does not exceed 50 cm^3 of each component.

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