MEASUREMENTS OF THE EXCESS VOLUME OF BENZENE–METHANOL, BENZENE–ACETONITRILE AND METHANOL–ACETONITRILE MIXTURES BY A VIBRATING-TUBE DENSIMETER

Ivan CIBULKA, Vladimír HYNEK, Robert HOLUB and Jiří PICK

Department of Physical Chemistry,
Prague Institute of Chemical Technology, 166 28 Prague 6

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A digital vibrating-tube densimeter was constructed for measuring the density of liquids at several temperatures. The underlying principle of the apparatus is the measurement of the period of eigenvibrations of a V-shaped tube; the second power of the period of the vibrations is proportional to the density of the liquid in the tube. The temperature of the measuring system is controlled by an electronic regulator. The mean error in the density measurement is approximately $\pm 1 \cdot 10^{-5}$ g cm^{-3} at 25°C and $\pm 2 \cdot 10^{-5}$ g cm^{-3} at 40°C.

The apparatus was used for an indirect measurement of the excess volume, tested with the benzene–cyclohexane system and further used for determining the excess volume of the benzene–methanol, benzene–acetonitrile and methanol–acetonitrile systems at 25 and 40°C.

Reliable data on the density or excess volume of benzene–methanol, benzene–acetonitrile and methanol–acetonitrile mixtures are extremely scarce in the literature. Data on the density of benzene–methanol mixtures at 25°C had been reported by Scatchard and coworkers[33], Scatchard and Ticknor[32] and Washburn and Lightbody[40], the excess volume at 25, 35 and 45°C had been measured by Brown and Smith[4]. More detailed data are available for the benzene–acetonitrile system[1,5,7,26] at temperatures of 20, 25, 30 and 45°C, however, only few data can be found for the methanol–acetonitrile system[22,29,39] at 0, 25 and 30°C. Composition dependences of the excess volume of these systems are of a relatively rarely encountered type, *i.e.* they display one point of inflexion. The systems studied are also interesting from the point of view of the nature of components present, *i.e.* nonpolar benzene, associating methanol and highly polar acetonitrile. Therefore it is desirable to determine concentration dependences of the excess volume in these mixtures in more detail and to supplement the scarce literature data.

Many methods had been elaborated for measuring the excess volume in liquid mixtures, an excellent survey was presented *e.g.* by Battino[2]. One group among these methods is formed by indirect methods, in which the excess volume is calculated from values of the density of the mixture and its pure components and main emphasis is concentrated on the precise density measurement. Owing to accuracy requirements on the measurements, the classical pycnometric determination of the liquid loses here somewhat its significance and the attention is being paid to more accurate methods, *i.e.* to magnetic float devices and recently mainly to the vibrating-tube densimeter. Three construction types of this densimeter had been reported in the literature. Kratky, Leopold and Stabinger[16–18,20,34] had described a construction which became a basis of the industrially produced apparatus by A. Paar KG Co., Graz, Austria (*e.g.* DMA 02C and DMA 10 models). Picker, Tremblay and Jolicoeur[27] had developed a flow apparatus with thermostating of the liquid investigated (commercially it appeared as the 02D model by the Canadian SODEV Inc.). Henning and Hieke[11] had constructed a vibrating-tube densimeter for an automatic analysis. Principles of these devices are identical, differences can be found in the material of the vibrating tube (glass or steel), in the manner of initiation and maintaining of its vibrations and in the electronic circuits. The temperature control of the tube is in all cases achieved by a double jacket, through which the thermostating liquid from the bath is flowing. The accuracy in the density measurement as reported by the authors is $10^{-5}-10^{-6}$ g cm^{-3}. Advantages of this method for measuring the liquid density are: high accuracy and easy performance, digitally indicated data, a possibility of flow measurements and, not in the last place, a considerable amount of possible applications (*e.g.*, continual analytical measurements, remote density measurements for controlling and checking purposes, *etc.*).

It was the aim of our work to construct a digital vibrating-tube densimeter for liquids, to test it and to determine the concentration dependence of the excess volume of benzene–methanol, benzene–acetonitrile and methanol–acetonitrile mixtures at temperatures of 25 and 40°C. A special attention has been given to the estimation of error in experimental data.

EXPERIMENTAL

Apparatus

The fundamental measuring system of the apparatus is a V-shaped glass tube. Mechanical vibrations of the tube are registered by a photoelectric sensor. The signal from this photoelectric sensor is, after amplification, phase adjustment and stabilization of amplitude, fed to an exciting coil, whose magnetic field acts on a ferrite target sticked on the tube. At a suitable adjustment of the phase shift of the signal, vibrations of the tube are undamped and their period τ depends on the density of the liquid in the tube, ϱ, through the relation $\varrho = A\tau^2 + B$, where constants A and B can be determined by calibration. The period τ is measured by means of a Tesla BM 520 counter. The frequency of oscillations of the tube filled with air is roughly 277 Hz, for water it is 219 Hz (at 25°C). The experiments were performed by the static method (no flow of the liquid). The measuring system is placed in the cavity of a metal block, whose temperature is maintained electronically at the required value. The electronic regulator of temperature is in principle identical with that employed for the temperature control of calorimeters[37] and enables measurements at several preliminarily selected temperatures. The selection of temperature is performed by a push-button switch. The stability of the temperature inside the cavity of the metal block is better than ±0·005 K (determined by a Hewlett–Packard 2801 A quartz thermometer).

Calibration

It was found during the verification of validity of the linear relation between the density of the liquid in the tube and the square of the vibration period that, with the calibration inside a larger interval of density (air, water), the apparatus yields lower values of density. *E.g.*, for a liquid with the density of approximately 0·78 g cm^{-3}, the mean deviation was $8 \cdot 10^{-5}$ g cm^{-3}. This finding is in accordance with observation by Kiyohara and Benson[15] who had arrived at a similar conclusion during the investigation of properties of a commercial DMA 02C apparatus with a glass tube. This phenomenon has not been described with the apparatus by Picker and coworkers[27] (stainless tube), where, on the contrary, it had been found that the experimental accuracy is independent of the width of the calibration interval within relatively large limits[8,27]. Therefore it can be deduced that this property of the constructed apparatus is inherent to glass tubes.

During the measurements, the apparatus was calibrated for each of the systems investigated with the corresponding pure components. The calibration was always checked after 3—4 measurements with mixtures. As it will be shown later, this method of calibration yields an error in the mixture density which is equal or lower than that in the density of calibration liquids but the effect of the uncertainty in densities of these liquids on values of the excess volume is negligible for most systems investigated. Densities of calibration liquids (pure components) were determined pycnometrically by an Ostwald–Sprengel bicapillary pycnometer with a volume of 10 cm^3.

Method of Measurement

Mixtures investigated were prepared by weighing of partially degassed components. Flasks with an inner volume of 10 cm^3 were always filled with $\sim$6 cm^3 of a mixture and closed with a closure containing a silicon rubber membrane. The filling with components and withdrawal of mixtures were performed by hypodermical syringes without opening the flasks.

In measurements at 25°C, the apparatus was filled with liquids whose temperature was identical with that of the surroundings, *i.e.* $\sim$20°C. In measurements at 40°C, the liquids investigated were preheated in an air thermostat to a temperature close to 40°C and then transferred to the measuring tube.

The standard frequency of the Tesla BM 520 counter is 10 MHz. For the uncertainty due to the standard frequency to appear only in the eighth digit of the resulting value, it is necessary to multiply the vibration period by at least 10^4 before the measurement. In the measurements, the period was multiplied by the coefficient of $2 \,.\, 10^4$ and the time of one measurement of the period was 88 s on the average.

Materials Used

Thiophene-free benzene was refluxed for 8 hours with metallic sodium and then rectified on a 60-plate bubble-cap column separated from the air humidity. Cyclohexane, A. R. grade, was shaken with a mixture of HNO_3 and concentrated H_2SO_4 to remove traces of benzene. Then it was washed with an aqueous solution of Na_2CO_3 and water and dried with anhydrous $CuSO_4$. The product was rectified on the 60-plate bubble-cap column separated from the air humidity. Methanol, A.R. grade, was refluxed for 8 hours with Grignard reagent ($Mg + I_2$). The dried product was rectified on the 60-plate bubble-cap column separated from the air humidity. Acetonitrile, A.R. grade, was refluxed for several hours with a small amount of aqueous KOH to remove traces of acrylonitrile. Then it was rectified on a 150 cm-long column packed with stainless helices. The content of impurities, as determined by gas chromatography and mass spectrometry, was in all substances lower than 0·1%. The density of substances agrees with values reported in the literature; benzene: $\varrho_4^{25} = 0{\cdot}87347$ (lit. 0·87347—0·87372), $\varrho_4^{40} = 0{\cdot}85759$ (lit. 0·85771); cyclohexane: $\varrho_4^{25} = 0{\cdot}77387$ (lit. 0·77322—0·77397), $\varrho_4^{40} = 0{\cdot}75991$ (lit. 0·75999); methanol: $\varrho_4^{25} = 0{\cdot}78670$ (lit. 0·78655—0·78676), $\varrho_4^{40} = 0{\cdot}77228$ (lit. 0·77234); acetonitrile: $\varrho_4^{25} = 0{\cdot}77669$ (lit. 0·77664), $\varrho_4^{40} = 0{\cdot}76054$ (lit. 0·76127).

Calculation of the Density and Excess Volume; Estimation of Error in the Measurement

If, for each of the two-component mixtures, the apparatus is calibrated with the corresponding pure components. The density of the mixture is given by

$$\varrho = \varrho_2 + \frac{\tau^2 - \tau_2^2}{\tau_1^2 - \tau_2^2} (\varrho_1 - \varrho_2) , \tag{1}$$

where ϱ, τ, ϱ_1, τ_1, ϱ_2, τ_2 are densities and vibration periods of the mixture, component 1 and component 2, resp. The molar excess volume is equal to

$$v^{\mathrm{E}} = \frac{x_1 M_1 + (1 - x_1) M_2}{\varrho} - \frac{x_1 M_1}{\varrho_1} - \frac{(1 - x_1) M_2}{\varrho_2} , \tag{2}$$

where x_1 is the mole fraction of component 1 ($x_1 = (m_1/M_1)/(m_1/M_1 + m_2/M_2)$) and M_i is the molecular weight of component i.

Densities of pure components were determined pycnometrically and in calculations by Eqs (*1*) and (*2*) they were taken as constants at the corresponding temperature. Therefore we can distinguish between two "types" of experimental error: *1*) a scatter of values around certain composition dependences of the density and excess volume, which results from errors in the input quantities m_1, m_2, τ_1, τ_2, τ. Errors in these quantities can be mutually compensated and so this scatter (in the following denoted as $\delta\varrho$ and δv^{E}) may be estimated by statistical methods; *2*) a deviation of these dependences from "correct" ones, which is given by the error in the pycnometric determination of density of pure components. For estimating the magnitude of this deviation (denoted as $\Delta\varrho$ and Δv^{E}) in the most unfavourable case, it is suitable to use a linear estimation. These arguments then lead to the following expressions.

$$\delta\varrho \approx \left[\left(\frac{\partial\varrho}{\partial\tau_1}\right)^2 (\delta\tau_1)^2 + \left(\frac{\partial\varrho}{\partial\tau_2}\right)^2 (\delta\tau_2)^2 + \left(\frac{\partial\varrho}{\partial\tau}\right)^2 (\delta\tau)^2\right]^{1/2} , \tag{3}$$

$$\delta v^{\mathrm{E}} \approx \left[\left(\frac{\partial v^{\mathrm{E}}}{\partial\tau_1}\right)^2 (\delta\tau_1)^2 + \left(\frac{\partial v^{\mathrm{E}}}{\partial\tau_2}\right)^2 (\delta\tau_2)^2 + \left(\frac{\partial v^{\mathrm{E}}}{\partial\tau}\right)^2 (\delta\tau)^2 + \left(\frac{\partial v^{\mathrm{E}}}{\partial m_1}\right)^2 (\delta m_1)^2 + \left(\frac{\partial v^{\mathrm{E}}}{\partial m_2}\right)^2 (\delta m_2)^2\right]^{1/2} , \tag{4}$$

$$\Delta\varrho \leqq \left|\left(\frac{\partial\varrho}{\partial\varrho_1}\right) \delta\varrho_1\right| + \left|\left(\frac{\partial\varrho}{\partial\varrho_2}\right) \delta\varrho_2\right| , \tag{5}$$

$$\Delta v^{\mathrm{E}} \leqq \left|\left(\frac{\partial v^{\mathrm{E}}}{\partial\varrho_1}\right) \delta\varrho_1\right| + \left|\left(\frac{\partial v^{\mathrm{E}}}{\partial\varrho_2}\right) \delta\varrho_2\right| . \tag{6}$$

RESULTS

As a testing system for methods of determination of the excess volume, the benzene–cyclohexane mixture is usually recommended[28]. Experimental values of the density and excess volume in this system are in Table *I*. The concentration dependence of the excess volume was correlated by the Redlich–Kister expansion[31], the number of necessary parameters (Table IV) obtained by the least squares method was determined by a statistical test (*F*-test). The correlated dependences were compared with literature data, Table II contains values of the mean quadratic deviation between litera-

TABLE I

Density and Excess Volume of the Benzene(1)–Cyclohexane(2) System

x_1	ϱ $g . cm^{-3}$	v^E $cm^3 . mol^{-1}$	x_1	ϱ $g . cm^{-3}$	v^E $cm^3 . mol^{-1}$
			25°C		
0·05961	0·777704	0·1495	0·48248	0·811756	0·6510
0·10462	0·780736	0·2522	0·49600	0·813069	0·6502
0·10588	0·780843	0·2521	0·52033	0·815446	0·6489
0·11278	0·781321	0·2666	0·52771	0·816174	0·6482
0·11482	0·781451	0·2725	0·59994	0·823598	0·6195
0·15692	0·784436	0·3551	0·63304	0·827161	0·5960
0·17340	0·785665	0·3808	0·72290	0·837223	0·5163
0·18367	0·786421	0·3986	0·72946	0·838023	0·5047
0·19511	0·787251	0·4204	0·76808	0·842629	0·4537
0·25513	0·791903	0·5028	0·81342	0·848169	0·3902
0·29698	0·795270	0·5516	0·83122	0·850418	0·3606
0·37361	0·801756	0·6166	0·87088	0·855563	0·2871
0·37775	0·802135	0·6171	0·90995	0·860774	0·2094
0·41540	0·805507	0·6348	0·91626	0·861655	0·1936
0·46023	0·809656	0·6468	0·95781	0·867365	0·1062
			40°C		
0·05744	0·763570	0·1410	0·52749	0·801363	0·6616
0·10170	0·766459	0·2485	0·59669	0·808306	0·6369
0·14225	0·769200	0·3388	0·62948	0·811772	0·6120
0·19129	0·772725	0·4254	0·71601	0·821259	0·5332
0·28220	0·779698	0·5476	0·78879	0·829794	0·4343
0·32714	0·783314	0·5963	0·86294	0·838971	0·3116
0·37514	0·787358	0·6327	0·93263	0·848193	0·1623
0·46305	0·795240	0·6623	—	—	—

ture and our experimental data. At 25°C, the agreement with most literature data is good, an excellent agreement was achieved with data reported by Stokes and coworkers[35], Kumaran and McGlashan[19], Oba and coworkers[25] and Kiyohara and Benson[15]. Considerable deviations are exhibited by data measured by Chareyron

TABLE II

The Comparison of Experimental and Literature Values of the Excess Volume v^E ($cm^3 . mol^{-1}$) for the Benzene–Cyclohexane System

Method	$\Delta . 10^{3a}$	Sign of $v^E_{lit} - v^E_{exp}$	Author (ref.)
	25°C		
Dilatometer	8·4	−	Powell(28)
Dilatometer	2.6	+ −	Stookey(36)
Dilatometer	4·6	+ −	Letcher(21)
Dilatometer	4·0	+ −	Gracia(9)
Dilatometer	4·1	+ −	Dickinson(6)
Dilatometer	3·0	+	Tanaka(38)
Dilatometer	0·7	+ −	Stokes(35)
Piston dilat.	1·3[b]	+ −	Stokes(35)
Dilatometer	1·3	+ −	Kumaran(19)
Dilatometer	9·3	−	Watson(41)
Dilatometer	6·6	−	Beath(3)
Dilatometer	10·8	−	Chareyron(12)
Dilatometer	10·9	−	Janssens(13)
Pycnometer	3·0[c]	+ −	Wood(43)
Pycnometer	1·7	+ −	Oba(25)
Magn. float	2·9	+	Weeks(42)
Vibr. dens.	3·6	+ −	Grolier(10)
Vibr. dens.	2·2	+ −	Kiyohara(15)
Vibr. dens.	4·6	+ −	Goates(8)
Vibr. dens.	3·8[b]	+ −	Meyer(23)
Vibr. dens.	5·7	+ −	Radojkovič(30)
	40°C		
Dilatometer	26·2	+ −	Powell(28)
Dilatometer	20·2	+ −	Nigam(24)
Pycnometer	18·2	+ −	Woycicki(44)
Pycnometer	4·6[b]	−	Wood(43)

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[a] $\Delta = [\int_0^1 (v^E_{lit} - v^E_{exp})^2 \, dx_1]^{1/2}$, where v^E_{lit} and v^E_{exp} are values calculated from the corresponding correlations (*i.e.*, from relations reported by the authors and those indicated in Table IV); [b] Our correlations of the literature data (by the Redlich–Kister relation[31]); [c] v^E_{lit} from the relation reported by Kumaran and McGlashan[19].

and Clechet[12], Janssens and Ruel[13] and others[28,41]. It is difficult to explain these differences, however, we may at least mention the fact that the deviations are negative and that all the latter data were obtained by dilatometers. There is a lack of data on this system at 40°C in the literature and considerable mutual differences exist among available ones. Our data are in a relatively good agreement with those by Wood and Austin[43], the agreement with others is worse.

Our experimental data on the density and excess volume of the benzene–methanol, benzene–acetonitrile and methanol–acetonitrile systems are in Table III. The mole fraction and density are given with an accuracy up to the fifth and sixth digit beyond the decimal point, respectively, to reduce the effect of rounding errors in calculations of the excess volume. The concentration dependences of the excess volume were correlated by the Redlich–Kister expansion[31]

$$v^{E} = x_1 x_2 \sum_{i=1}^{N} A_i (1 - 2x_1)^{i-1} \tag{7}$$

and by a relation recommended by Jones and coworkers[14] for dependences with a point of inflexion

$$v^{E} = x_1 x_2 \sum_{i=1}^{N} A_i x_2^{(i-1)/2} \,. \tag{8}$$

Each dependence was correlated by the most suitable relation selected according to the criterion of the corresponding standard deviation and the necessary number of parameters (determined also by the *F*-test). Parameters in these relations as determined by the least squares method are in Table IV. It was found by an analysis of Eqs (*7*) and (*8*), their practical application to experimental dependences and a mutual comparison that relation (*8*) is more sensitive to the accuracy of the calculations (to rounding errors) during the solution of the set of normal equations. Similarly, the highest usable number of parameters in relation (*8*) is, at a constant accuracy of the calculations, lower and the parameters are mutually more interrelated than in the case of relation (*7*). On the other side, however, relation (*8*) is more appropriate for correlations of strongly asymmetrical dependences (*e.g.* benzene–methanol, for which relation (*7*) failed completely).

The estimate of the experimental error was performed for all measurements at 25°C including the benzene–cyclohexane system. It can be assumed that $|\delta\tau_1| = |\delta\tau_2| = |\delta\tau|$, $|\delta m_1| = |\delta m_2| = |\delta m|$ and $|\delta\varrho_1| = |\delta\varrho_2| = |\delta\varrho_p|$. The errors in the invidual input quantities were estimated as $|\delta\tau| = 9 \,.\, 10^{-9}$ s (including the effect of temperature oscillations in the measuring system), $|\delta m| = 7 \,.\, 10^{-4}$ g (weighing error and losses due to evaporation into the vapour space of the weighing flask) and $|\delta\varrho_p| = 5 \,.\, 10^{-5}\ \text{g}\,.\,\text{cm}^{-3}$ (error due to the pycnometric determination of density

TABLE III

Density and Excess Volume of the Binary Systems

x_1	ϱ g . cm^{-3}	v^E cm^3 . mol^{-1}	x_1	ϱ g . cm^{-3}	v^E cm^3 . mol^{-1}
Benzene(1)–methanol(2), 25°C					
0·03701	0·793539	−0·0057	0·64132	0·855609	0·0190
0·07833	0·800541	−0·0120	0·70878	0·859501	0·0237
0·13393	0·808954	−0·0163	0·75106	0·861749	0·0288
0·18175	0·815440	−0·0191	0·78122	0·863330	0·0278
0·22749	0·821052	−0·0189	0·78717	0·863617	0·0293
0·26093	0·824856	−0·0185	0·79586	0·864016	0·0329
0·32695	0·831657	−0·0132	0·84872	0·866581	0·0335
0·35027	0·833872	−0·0109	0·85215	0·866749	0·0329
0·38326	0·836892	−0·0099	0·85548	0·866923	0·0312
0·41935	0·840040	−0·0107	0·88454	0·868249	0·0321
0·46616	0·843727	−0·0015	0·91209	0·869503	0·0292
0·47596	0·844491	−0·0015	0·92121	0·869921	0·0271
0·52204	0·847854	0·0048	0·94863	0·871112	0·0249
0·57220	0·851297	0·0090	0·96145	0·871654	0·0241
0·62397	0·854578	0·0154	0·98182	0·872545	0·0182
Benzene(1)–methanol(2), 40°C					
0·03591	0·778828	−0·0066	0·58583	0·836387	0·0339
0·08146	0·786346	−0·0106	0·63752	0·839646	0·0326
0·17449	0·799575	−0·0173	0·71235	0·843875	0·0402
0·23843	0·807176	−0·0110	0·76750	0·846717	0·0478
0·31373	0·815128	−0·0095	0·84781	0·850647	0·0466
0·38503	0·821631	0·0008	0·92381	0·854094	0·0396
0·47953	0·829172	0·0137	0·94454	0·854972	0·0388
0·52595	0·832451	0·0234			
Benzene(1)–acetonitrile(2), 25°C					
0·02273	0·780187	0·0101	0·47984	0·836171	−0·0433
0·04569	0·783596	0·0227	0·51135	0·839176	−0·0561
0·07399	0·787723	0·0333	0·55480	0·843127	−0·0704
0·10435	0·792081	0·0376	0·59263	0·846452	−0·0847
0·13242	0·795958	0·0417	0·65257	0·851412	−0·1015
0·15858	0·799467	0·0442	0·69568	0·854770	−0·1101
0·19497	0·804253	0·0408	0·72588	0·857033	−0·1151
0·22158	0·807610	0·0392	0·76382	0·859726	−0·1156
0·25832	0·812136	0·0321	0·80484	0·862489	−0·1117
0·29791	0·816837	0·0217	0·81581	0·863192	−0·1088
0·30323	0·817443	0·0210	0·85977	0·865949	−0·0982
0·32949	0·820454	0·0120	0·88397	0·867371	−0·0873

TABLE III
(*Continued*)

x_1	ϱ g . cm^{-3}	v^E cm^3 . mol^{-1}	x_1	ϱ g . cm^{-3}	v^E cm^3 . mol^{-1}
0·37040	0·824980	−0·0026	0·91803	0·869307	−0·0704
0·42306	0·830496	−0·0196	0·94557	0·870776	−0·0512
0·43850	0·832100	−0·0283	0·97407	0·872191	−0·0244
Benzene(1)–acetonitrile(2), 40°C					
0·04696	0·767784	0·0135	0·59457	0·830973	−0·1221
0·09813	0·775222	0·0262	0·65018	0·835565	−0·1363
0·15874	0·783635	0·0247	0·68639	0·838391	−0·1421
0·22511	0·792226	0·0172	0·75103	0·843144	−0·1465
0·29806	0·801116	−0·0069	0·81595	0·847506	−0·1371
0·36793	0·809033	−0·0353	0·88853	0·851797	−0·0963
0·45402	0·817996	−0·0701	0·92643	0·853950	−0·0768
0·53606	0·825798	−0·1010			
Methanol(1)–acetonitrile(2), 25°C					
0·03751	0·777096	−0·0091	0·48163	0·783124	−0·1367
0·04983	0·777258	−0·0134	0·51280	0·783541	−0·1421
0·09276	0·777800	−0·0265	0·54285	0·783917	−0·1454
0·12966	0·778293	−0·0390	0·56811	0·784251	−0·1490
0·14845	0·778551	−0·0456	0·60369	0·784696	−0·1521
0·16212	0·778725	−0·0494	0·65032	0·785239	−0·1531
0·19307	0·779164	−0·0607	0·68335	0·785612	−0·1527
0·22531	0·779613	−0·0714	0·72430	0·786037	−0·1495
0·25164	0·779970	−0·0792	0·76203	0·786378	−0·1434
0·29712	0·780595	−0·0925	0·79999	0·786657	−0·1333
0·31673	0·780865	−0·0980	0·83185	0·786851	−0·1224
0·34309	0·781227	−0·1050	0·87095	0·787053	−0·1068
0·38678	0·781804	−0·1146	0·90309	0·787096	−0·0873
0·41249	0·782189	−0·1227	0·93634	0·787066	−0·0631
0·43811	0·782531	−0·1278	0·97117	0·786918	−0·0318
Methanol(1)–acetonitrile(2), 40°C					
0·04981	0·761145	−0·0119	0·64687	0·769739	−0·1404
0·09073	0·761644	−0·0200	0·72101	0·770681	−0·1373
0·15132	0·762466	−0·0363	0·76815	0·771231	−0·1313
0·19819	0·763122	−0·0491	0·82519	0·771848	−0·1202
0·29366	0·764513	−0·0757	0·86515	0·772111	−0·1023
0·38048	0·765805	−0·0977	0·89283	0·772253	−0·0876
0·47159	0·767185	−0·1184	0·94049	0·772434	−0·0583
0·56510	0·768575	−0·1336			

TABLE IV

Parameters A_i (cm^3 . mol^{-1}) in the Correlations for the Experimental Composition Dependences of the Excess Volume

System	t, °C	Correlation, Eq.	A_1	A_2	A_3	A_4	$\sigma(v^E)$
C_6H_6(1)–C_6H_{12}(2)	25	7	2·60052 ± 0·00217	0·10378 ± 0·00951	0·02744 ± 0·00895	−0·04813 ± 0·02211	0·0017
	40	7	2·66546 ± 0·00490	0·10154 ± 0·01287	—	—	0·0035
C_6H_6(1)–CH_3OH(2)	25	8	1·10065 ± 0·07257	−3·45038 ± 0·37769	4·03229 ± 0·62980	−1·89816 ± 0·33803	0·0019
	40	8	1·46267 ± 0·15928	−4·52203 ± 0·82251	5·50732 ± 1·36524	−2·68304 ± 0·72779	0·0029
C_6H_6(1)–CH_3CN(2)	25	7	−0·20525 ± 0·00143	0·77626 ± 0·00533	−0·04690 ± 0·00606	0·06587 ± 0·01320	0·0010
	40	7	−0·35329 ± 0·00465	0·82096 ± 0·00897	−0·04518 ± 0·02052	—	0·0025
CH_3OH(1)–CH_3CN(2)	25	7	−0·55816 ± 0·00088	0·32357 ± 0·00346	−0·15533 ± 0·00394	0·14303 ± 0·00871	0·0007
	40	8	−1·36505 ± 0·02110	1·42932 ± 0·06725	−0·27979 ± 0·05160	—	0·0010

TABLE V

Estimated Errors in the Density and Excess Volume for the Measurements at 25°C

System	$\delta\varrho \cdot 10^5$ g . cm^{-3}	$\delta v^E \cdot 10^3$ cm^3 . mol^{-1}	$\Delta\varrho_{max} \cdot 10^5$ g . cm^{-3}	$\Delta v^E_{max} \cdot 10^3$ cm^3 . mol^{-1}
C_6H_6–C_6H_{12}	1·3	2·1	5·0	0·3
C_6H_6–CH_3OH	1·3	1·4	5·0	0·2
C_6H_6–CH_3CN	1·3	1·5	5·0	0·3
CH_3OH–CH_3CN	1·3	0·8	5·4	1·5

of pure components). Mean values of the estimated errors of density and excess volume can be found in Table V. Obviously, estimated values of δv^E correspond approximately with values of the standard deviation from the correlations. A low value of δv^E in the methanol–acetonitrile system is a consequence of an extremely weak dependence of the error in the excess volume of this system on the weighing error of components. The system benzene–cyclohexane is most sensitive to the weighing error. The maximum error in the excess volume due to the uncertainty in values of density of pure components (Δv^E) can be – with respect to errors caused by the uncertainty in other input quantities – neglected for all of the systems investigated except the methanol–acetonitrile one.

A similar analysis and estimation of the experimental error can be performed for the temperature of 40°C. The errors of values measured at this temperature are higher than those at 25°C. This increase can be related to greater changes in the mixture composition (increase in δm), to a lower temperature stability (increase in $\delta \tau$) and, not in the last place, probably to a higher error in the determination of density of calibration liquids (increase in $\delta \varrho_p$).

Our experimental results show that the apparatus constructed can be used for determining the liquid density with the accuracy of $\pm 2 \,.\, 10^{-3}\%$. The accuracy of values of the excess volume is comparable with that yielded by similar apparatuses as described in the literature.

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REFERENCES

1. Absood A. H., Tutunji M. S., Hsu K.-Y., Clever H. L.: J. Chem. Eng. Data *21*, 304 (1976).
2. Battino R.: Chem. Rev. *71*, 5 (1971).
3. Beath L. A., O'Neil S. P., Williamson A. G.: J. Chem. Thermodyn. *1*, 293 (1969).
4. Brown I., Smith F.: Aust. J. Chem. *15*, 1 (1962).
5. Brown I., Smith F.: Aust. J. Chem. *15*, 9 (1962).
6. Dickinson E., Hunt D. C., McLure I. A.: J. Chem. Thermodyn. *7*, 731 (1975).
7. Friedel B., Raetzsch M. T.: Wiss. Z. Tech. Hochsch. "Carl Schorlemmer", Leuna Merseburg *15*, 333 (1973).
8. Goates J. R., Ott J. B., Moellmer J. F.: J. Chem. Thermodyn. *9*, 249 (1977).
9. Gracia M., Otin S., Gutierez Losa C.: J. Chem. Thermodyn. *7*, 293 (1975).
10. Grolier J.-P. E., Ballet D., Viallard A.: J. Chem. Thermodyn. *6*, 895 (1974).
11. Henning G., Hieke E.: Fresenius' Z. Anal. Chem. *265*, 97 (1973).
12. Chareyron R., Clechet P.: Bull. Soc. Chim. Fr. *2853* (1971).
13. Janssens J. M., Ruel M.: Can. J. Chem. Eng. *50*, 591 (1972).
14. Jones D. E. G., Ian A. W., Anand S. C., Wetmore A. R. W., Benson G. C.: J. Chem. Eng. Data *17*, 501 (1972).
15. Kiyohara O., Benson G. C.: Can. J. Chem. *51*, 2489 (1973).
16. Kratky O., Leopold H., Stabinger H.: Z. Angew. Phys. *27*, 273 (1969).
17. Kratky O., Leopold H., Stabinger H.: U.S. No 3 523 446 (Cl. G 01 N, 9-00), Austrian No 280 662, Brit. No 13 242/68, Fr. No 1 579 521, Ger. No 1 648 953.

18. Kratky O., Leopold H., Stabinger H.: Methods Enzymol. *27* (Pt. D), 98 (1973).
19. Kumaran M. K., McGlashan M. L.: J. Chem. Thermodyn. *9*, 259 (1977).
20. Leopold H.: Elektronik *19*, 297 (1970).
21. Letcher T. M.: J. Chem. Thermodyn. *7*, 205 (1975).
22. Mato F., Fernandez-Polanco F.: An. Quim. *71*, 815 (1975).
23. Meyer R., Giusti G., Meyer M., Vincent E.-J.: Thermochim. Acta *13*, 379 (1975).
24. Nigam R. K., Singh P. P.: Trans. Faraday Soc. *65*, 950 (1969).
25. Oba M., Murakami S., Fujishiro R.: J. Chem. Thermodyn. *9*, 407 (1977).
26. Palmer D. A., Smith B. D.: J. Chem. Eng. Data *17*, 71 (1972).
27. Picker P., Tremblay E., Jolicoeur C.: J. Solution Chem. *3*, 377 (1974).
28. Powell R. J., Swinton F. L.: J. Chem. Eng. Data *13*, 260 (1968).
29. Prasad N., Singh R., Prakash O., Prakash S.: Indian J. Pure Appl. Phys. *14*, 676 (1976).
30. Radejkovič N., Tasič A., Djordjevič B., Grozdanič D.: J. Chem. Thermodyn. *8*, 1111 (1976).
31. Redlich O., Kister T.: Ind. Eng. Chem. *40*, 345 (1948).
32. Scatchard G., Ticknor L. B.: J. Amer. Chem. Soc. *74*, 3724 (1952).
33. Scatchard G., Wood S. E., Mochel J. M.: J. Amer. Chem. Soc. *68*, 1957 (1946).
34. Stabinger H., Leopold H., Kratky O.: Monatsh. Chem. *98*, 436 (1967).
35. Stokes R. H., Levien B. J., Marsh K. N.: J. Chem. Thermodyn. *2*, 43 (1970).
36. Stookey D. J., Sallak H. M., Smith B. D.: J. Chem. Thermodyn. *5*, 741 (1973).
37. Svoboda V., Hynek V., Veselý F., Pick J.: This Journal *37*, 3165 (1972).
38. Tanaka R., Kiyohara O., D'Arcy P. J., Benson G. C.: Can. J. Chem. *53*, 2262 (1975).
39. Vincent, Delachanal 1880 — cit. by Timmermans J.: *Physico-Chemical Constants of Binary Systems in Concentrated Solutions*, Vol. 2. Interscience, London 1959.
40. Washburn E. R., Lightbody A.: J. Phys. Chem. *34*, 2701 (1930).
41. Watson A. E. P., MeLure I. A., Bennett J. E., Benson G. C.: J. Phys. Chem. *69*, 2753 (1965).
42. Weeks I. A., Benson G. C.: J. Chem. Thermodyn. *5*, 107 (1973).
43. Wood S. F., Austin A. E.: J. Amer. Chem. Soc. *67*, 480 (1945).
44. Woycicki W., Sadowska K. W.: Bull. Acad. Pol. Sci., Ser. Sci. Chim. *16*, 147 (1968).

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