241. *Densities of Some Binary Liquid Mixtures. Part I.*

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Densities at 25° of binary mixtures of water with dioxan, acetone, and pyridine, and of mixtures of ethanol and pyridine are reported.

For other work it was necessary to know accurately the densities of various binary mixtures over the complete concentration range. Such determinations had been made by other workers but, in general, agreement was poor and seldom was the range 0—100% adequately covered. The system dioxan–water from 35 to 100% of dioxan was investigated by Hovorka, Schaefer, and Dreisbach (*J. Amer. Chem. Soc.*, 1936, **58**, 2264); Geddes (*ibid.*, 1933, **55**, 4832), who covered a greater concentration range but in less detail, reported a minimum in the concentration–density curve at approximately 1% of water.

Aqueous solutions of pyridine were studied by Hartley, Thomas, and Applebey (*J.*, 1908, **93**, 538) and Dunstan, Thole, and Hunt (*J.*, 1907, **91**, 1728; 1908, **93**, 561). The latter authors also published densities of ethanolic solutions of pyridine (*loc. cit.*), and later work is reported by Hatem (*Bull. Soc. chim.*, 1949, **16**, 599).

Tabulated data for the acetone–water system at 25° were scarce, but two sets of figures were available at 20°, *viz.*, those of Naville (*Helv. Chim. Acta*, 1926, **9**, 913) and of Young (*J. Soc. Chem. Ind.*, 1933, **52**, 449). According to the International Critical Tables (1929) the densities of aqueous solutions of acetone can be calculated from the formula

$$d = d_w - 1{\cdot}171 \times 10^{-3}p_s - 9{\cdot}04 \times 10^{-6}p_s^2 - 5{\cdot}6 \times 10^{-9}p_s^3$$

where d = density of solution, d_w = density of water, and p_s = weight concentration of acetone.

For aqueous pyridine at 25·08°, Hartley, Thomas, and Applebey reported a continous variation of density with concentration, whereas Dunstan, Thole, and Hunt's results were

best represented by a series of discontinuous curves. Hartley *et al.* pointed out that, if the law of mass action holds, it is not possible for a homogeneous liquid mixture to show a discontinuous change of density with composition at constant temperature and pressure, unless there is a sudden change in the equilibrium constant of one of the systems.

The published data for ethanolic solutions of pyridine showed considerable discrepancies, and marked discontinuities in the concentration–density curves were reported.

It thus seemed desirable to carry out a complete investigation of these systems. All measurements were made at 25° ± 0·005°, and the values of d quoted in the following tables are with reference to water at 4°.

Two types of pyknometer of volumes between 10 and 25 c.c. were used, one being the conventional Sprengel type (see Partington, "An Advanced Treatise on Physical Chemistry," Vol. II, 1951, Longmans), the other based on a suggestion by D. I. Stock (private communication). The latter was simple in design, consisting essentially of two parallel vertical capillary tubes of unequal length, their lower ends being connected by a

1 : 4-Dioxan–water mixtures.

$C_4H_8O_2$, % (w/w)	d	Mean	$C_4H_8O_2$, % (w/w)	d	Mean	$C_4H_8O_2$, % (w/w)	d	Mean
0	0·99706		50·37	1·03261		90·72	1·02943	
	0·99705	0·99706		1·03255	1·03258		1·02937	1·02940
11·21	1·00605		59·96	1·03602		95·28	1·02840	
	1·00599	1·00602		1·03613	1·03607		1·02848	1·02844
20·10	1·01360		66·42	1·03702		99·06	1·02820	
	1·01370	1·01365		1·03694	1·03698		1·02812	1·02816
30·07	1·02105		69·82	1·03703		100·00	1·02806	
	1·02101	1·02103		1·03696	1·03700		1·02810	1·02808
39·68	1·02704		80·02	1·03490				
	1·02695	1·02700		1·03494	1·03492			

Pyridine–water mixtures.

C_5H_5N, % (w/w)	d	Mean	C_5H_5N, % (w/w)	d	Mean	C_5H_5N, % (w/w)	d	Mean
0	0·99707		35·58	1·00257		75·06	0·99967	
	0·99705	0·99706		1·00248	1·00253		0·99959	0·99963
5·07	0·99838		42·00	1·00281		82·03	0·99616	
	0·99833	0·99836		1·00280	1·00281		0·99605	0·99611
10·13	0·99937		50·21	1·00329		86·02	0·99307	
	0·99931	0·99938		1·00322	1·00326		0·99310	0·99309
19·86	1·00019		57·46	1·00311		89·38	0·98971	
	1·00014	1·00017		1·00303	1·00307		0·98979	0·98975
25·54	1·00166		59·38	1·00282		94·08	0·98467	
	1·00156	1·00161		1·00277	1·00280		0·98458	0·98463
30·05	1·00207		66·49	1·00208		100·00	0·97803	
	1·00201	1·00204		1·00216	1·00212		0·97797	0·97800

Pyridine-ethanol mixtures.

C_5H_5N, % (w/w)	d	Mean	C_5H_5N, % (w/w)	d	Mean	C_5H_5N, % (w/w)	d	Mean
0	0·78506		41·78	0·87214		80·07	0·94430	
	0·78510	0·78508		0·87205	0·87210		0·94422	0·94426
10·10	0·80444		50·06	0·88804		88·75	0·95957	
	0·80440	0·80442		0·88810	0·88807		0·95949	0·95953
20·93	0·82754		62·03	0·91186		100·00	0·97803	
	0·82748	0·82751		0·91178	0·91182		0·97797	0·97800
29·67	0·84713		69·11	0·92907				
	0·84705	0·84709		0·92898	0·92903			

Acetone–water mixtures.

$COMe_2$, % (w/w)	d	Mean	$COMe_2$, % (w/w)	d	Mean	$COMe_2$, % (w/w)	d	Mean
0	0·99706		39·98	0·93726		80·74	0·84210	
	0·99705	0·99706		0·93722	0·93724		0·84219	0·84205
9·82	0·98571		51·43	0·91406		89·15	0·81875	
	0·98574	0·98573		0·91398	0·91402		0·81864	0·81872
21·23	0·96937		60·49	0·89369		100·0	0·78512	
	0·96941	0·96939		0·89364	0·89367		0·78502	0·78507
29·62	0·95616		71·89	0·86582				
	0·95605	0·95611		0·86574	0·86578			

cylindrical bulb. The upper ends of the tubes were fitted with ground-glass caps and were at the same horizontal height so that the bulb was at an angle to both limbs. It was found that, if the apparatus was filled in the inverted position through the shorter limb no troublesome "air-locks" occurred. Most of the observations were made in duplicate with the latter type of pyknometer.

Discussion.—The data for the dioxan solutions agree well with those of Hovorka *et al.* and extend the work below 35% of dioxan. The minimum at 1% of water reported by Geddes was not found.

The results for the pyridine–water mixtures lie on a smooth curve and agree well with those of Hartley, Thomas, and Applebey, the temperature difference being taken into account.

Ethanolic solutions of pyridine proved to be the most difficult to investigate, as both liquids are very hygroscopic. A blank series of estimations showed variations of 4 and 5 units in the fourth place of decimals after solutions had been exposed to the atmosphere for 10 minutes. The results indicate that the density varies continuously with concentration.

The densities for aqueous solutions of acetone differed considerably from those given by the formula above. The results were plotted on a large scale, and the best curve was drawn. A set of simultaneous equations derived from points on this curve were solved to give a new equation:

$$d = 0{\cdot}99706 - 1{\cdot}091 \times 10^{-3}p_s - 9{\cdot}93 \times 10^{-6}p_s^2 - 3{\cdot}52 \times 10^{-9}p_s^3$$

The maximum difference between the experimental and calculated results was 0·0003.

Experimental

The organic solvent was distilled in all-glass apparatus directly into a roughly calibrated flask containing a known weight of conductivity water or alcohol under nitrogen. When the approximately correct volume had been collected the flask was re-weighed. The mixed solvent was transferred to the pyknometers either by blowing it over from the collecting flask through all-glass apparatus by means of dry nitrogen, or by "sucking" it over under reduced pressure.

The pyknometers were kept at 25° ± 0·005° and later weighed. All weighings were corrected to the vacuum standard and buoyancy corrections were made.

Owing to their hygroscopic nature, particular care was necessary when dealing with the organic solvents, and the pyknometers were kept stoppered or protected by drying tubes.

Materials.—The organic liquids were fractionally distilled at some stage in their purification and for this purpose 20-plate all-glass distillation columns were used (see Few and Smith, *J.*, 1949, 753).

Commercial 1 : 4-dioxan was fractionally distilled, and the middle fraction purified by repeated refluxing with sodium and fractional distillations (Kraus and Vingee, *J. Amer. Chem. Soc.*, 1934, **56**, 513), interposed with fractional crystallisations; the product had b. p. 101·40°/760 mm.

Commercial acetone was fractionally distilled and treated by Shipsey and Werner's method (*J.*, 1913, **103**, 1255) as modified by Livingston (*J. Amer. Chem. Soc.*, 1947, **69**, 1220). The product was refluxed with potassium permanganate, dried (K_2CO_3), and distilled in a stream of dry nitrogen; it had b. p. 56·20°/760 mm.

Pyridine (commercial) was distilled, and the 113—116° fraction repeatedly refluxed with potassium permanganate and sodium hydroxide until the solution retained its characteristic colour. The product was then fractionally distilled in a stream of dry nitrogen and dried over ignited barium oxide; it had b. p. 114·48°/760 mm.

Ethanol (99%) was treated by Donner and Hildebrand's method (*J. Amer. Chem. Soc.*, 1922, **44**, 2824) for the removal of aldehydes and heated under reflux over fresh lime. The product was boiled with anhydrous copper sulphate whilst a stream of nitrogen was passed through it, and finally redistilled over amalgamated aluminium chippings; it had b. p. 78·30°/760 mm.

All solvents were stored under nitrogen in sealed glass containers and redistilled in a stream of nitrogen immediately before use.

The water used in the mixtures was good-quality conductivity water.

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