

*Densities of Some Binary Liquid Mixtures. Part II.**

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Densities of methanol-water and 1 : 4 dioxan-ethanol at 25° are reported, and in the latter system there are considerable differences from previously published data. Attempts to interpret molecular interaction from partial molal volume-mol. fraction curves are described.

THIS work extends that previously described in Part I * to two further systems.

Aqueous methanol solutions have been studied at various temperatures by many workers (*e.g.*, Klasen and Norlin at 15°, *Arkiv Kemi, Min., Geol.*, 1905—07, II, No. 27; International Critical Tables, 1929, at 20°; Subnis, Bhagwat, and Kanugo, *J. Indian Chem. Soc.*, 1948, 25, 575, at 30°, 40°, and 50°) but accurate data at 25° over the entire concen-

1 : 4 Dioxan-ethanol

C ₄ H ₈ O ₂			C ₄ H ₈ O ₂			C ₄ H ₈ O ₂			C ₄ H ₈ O ₂		
(w/w)	<i>d</i>	Mean	(w/w)	<i>d</i>	Mean	(w/w)	<i>d</i>	Mean	(w/w)	<i>d</i>	Mean
0	0.78506	0.78508	24.89	0.83532	0.83529	57.36	0.90867	0.90862	88.93	0.99360	0.99360
	0.78510			0.83525			0.90857			0.99359	
1.24	0.78753	0.78751	31.26	0.84887	0.84882	60.18	0.91567	0.91565	90.91	0.99970	0.99969
	0.78749			0.84878			0.91562			0.99968	
2.73	0.79046	0.79045	34.87	0.85669	0.85668	63.26	0.92332	0.92330	93.76	1.00808	1.00807
	0.79044			0.85666			0.92328			1.00805	
5.48	0.79589	0.79589	41.26	0.87082	0.87082	69.00	0.93864	0.93862	95.82	1.01483	1.01480
	0.79589			0.87081			0.93860			1.01478	
7.92	0.80076	0.80074	44.17	0.87740	0.87737	72.06	0.94630	0.94627	98.13	1.02202	1.02199
	0.80073			0.87735			0.94625			1.02196	
13.67	0.81238	0.81234	49.05	0.88860	0.88858	79.13	0.96532	0.96530	99.20	1.02518	1.02517
	0.81230			0.88857			0.96529			1.02516	
16.37	0.81780	0.81779	52.12	0.89588	0.89588	84.26	0.97989	0.97988	100.00	1.02806	1.02808
	0.81777			0.89587			0.97987			1.02810	
20.43	0.82611	0.82608									
	0.82605										

* Part I, *J.*, 1952, 1326.

Methanol-water

CH ₃ ·OH			CH ₃ ·OH			CH ₃ ·OH			CH ₃ ·OH		
(w/w)	<i>d</i>	Mean	(w/w)	<i>d</i>	Mean	(w/w)	<i>d</i>	Mean	(w/w)	<i>d</i>	Mean
1.23	0.99465	0.99463	22.19	0.95985	0.95982	46.87	0.91827	0.91827	73.76	0.85811	0.85809
	0.99461			0.95979			0.91827			0.85808	
3.23	0.99100	0.99101	26.28	0.95319	0.95318	50.12	0.91203	0.91199	79.74	0.84431	0.84431
	0.99102			0.95318			0.91195			0.84430	
6.49	0.98566	0.98562	31.06	0.94524	0.94519	57.09	0.89789	0.89787	83.26	0.83599	0.83596
	0.98557			0.94515			0.89784			0.83593	
10.26	0.97878	0.97876	37.26	0.93445	0.93443	61.45	0.88707	0.88706	90.83	0.81463	0.81462
	0.97875			0.93441			0.88705			0.81460	
16.33	0.96878	0.96877	39.63	0.93162	0.93158	65.27	0.87865	0.87863	96.72	0.79649	0.79646
	0.96876			0.93154			0.87862			0.79643	
18.47	0.96607	0.96604	42.14	0.92700	0.92701	68.43	0.87144	0.87141	100.00	0.78655	0.78654
	0.96600			0.92703			0.87138			0.78653	

tration range appear to be scarce. Indeed the quoted values for the density of pure methanol at 25° range from 0.7864 to 0.7869 (Grinnell Jones and Forwalt, *J. Amer. Chem. Soc.*, 1938, **60**, 1683; Gibson, *ibid.*, 1935, **57**, 1551; Vosburgh, Connell, and Butler, *J.*, 1933, 935; Timmermans "Physico-chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950).

The densities of 1 : 4 dioxan-ethanol solutions have been determined by Hopkins, Yerger, and Lynch (*J. Amer. Chem. Soc.*, 1939, **61**, 2460) but since the value obtained for pure dioxan does not agree with that of the author (see Part I) it was felt necessary to reinvestigate the mixtures.

Consequently the two systems were carefully studied and the results are given in the annexed Table.

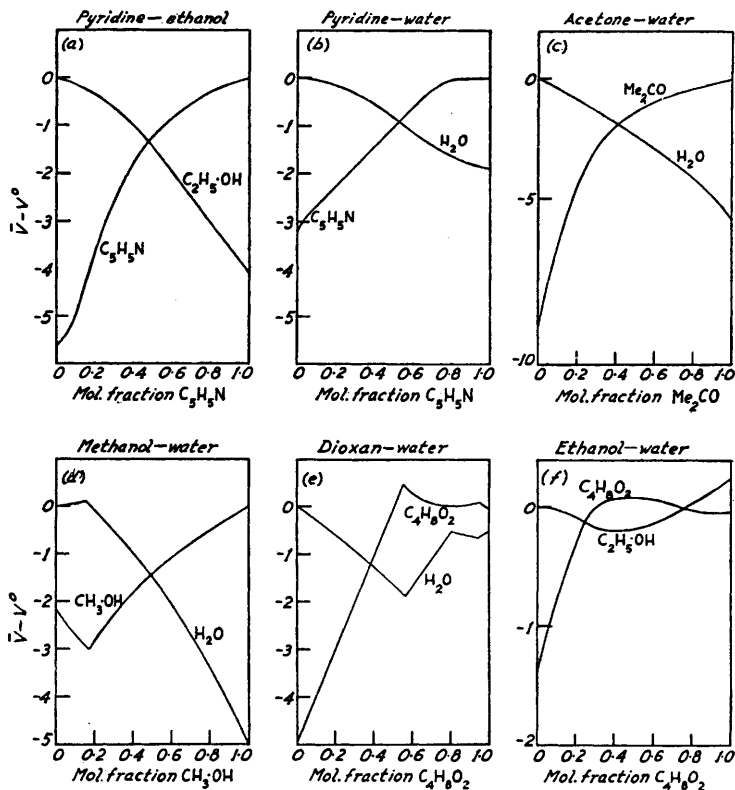
DISCUSSION

The results obtained for the methanol-water system lie on a smooth curve and agree reasonably well with those obtained by Gibson (*loc. cit.*).

The values obtained for dioxan-ethanol mixtures indicate that the density varies continuously with concentration. In the lower range of dioxan concentrations the results agree with those of Hopkins, Yerger, and Lynch (*loc. cit.*) but in higher range there is some disagreement.

From the results obtained in this work partial molal volume-mol. fraction curves were constructed by the method described by Lewis and Randall ("Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill, 1923, p. 38). This graphical method of intercepts, whilst not being the most accurate for the determination of partial molal quantities, gives the essential shape of the curves. For convenience the diagram shows $\bar{V} - V^0$ (where \bar{V} = partial molal volume, and V^0 = molal volume of the pure substance) plotted against the mol. fraction of one component. It can be seen that curves *a*, *b*, and *c* show certain similarities although the actual magnitude of the changes is greatest in the acetone-water system (*c*). Curve (*f*) shows that the partial molal volume of ethanol in dioxan solutions changes but little over the entire concentration range. However none of these curves show the sharp discontinuities exhibited by the methanol-water and dioxan-water systems. The former gives a curve very similar to the corresponding curve for the ethanol-water system (*idem, op. cit.*, p. 40) whilst the dioxan-water system (*e*) gives an unexpectedly complex curve (the break in the upper curve at approx. 0.84 mol. % of dioxan is not apparent on the scale used). Further, in this case, it must always be remembered that in the region where the curves show the most changes, the density is changing very slowly with concentration, and the experimental errors all but cover the variation. It was hoped that it might be possible to interpret the curves in terms of molecular association but no satisfactory explanation could be found. For example, if the type of curve obtained for ethanol-water and methanol-water systems be taken to indicate association then the same type of curve would be expected for the ethanol-dioxan

system since Freymann and Freymann (*Bull. Soc. chim.*, 1937, 4, 944) and Errera and Sack (*Trans. Faraday Soc.*, 1938, 33, 728) from infra-red measurements showed the characteristic OH frequency to be modified in such solutions. The latter authors also obtained



evidence of association in ethanol-pyridine mixtures, the curves of which are of an uncomplicated type.

Experimental.—The methods used were those described in Part I (*J.*, 1952, 1326).

Materials.—1 : 4-Dioxan and ethanol were purified by the methods described in Part I.

Commercial methanol was treated by the method of Bates, Mullaly, and Hartley (*J.*, 1923, 403) for the removal of aldehydes and ketones. The resulting alcohol was dried for several weeks over freshly-fired lime and fractionally distilled, the head and tail fractions being discarded. The middle fraction was distilled from metallic sodium immediately before use (Young and Fortey, *J.*, 1902, 717); it had b. p. $64.73^\circ/760$ mm.