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VISCOSITIES AND DENSITIES OF BENZENE–ACETIC ACID SOLUTIONS UP TO THEIR NORMAL BOILING POINTS

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In a continuing study in these laboratories, the physical properties of various binary liquid systems are being measured, to provide adequate data for an investigation of the effect of these properties on the contact efficiency of distillation. Some properties of the acetone–water system[1-3] and the methanol-toluene system[4] have previously been reported.

The literature reveals only limited measurements[5-8] of the viscosity and density of benzene–acetic acid solutions, and so the present study was begun.

Experimental

Materials.—"Baker Analyzed" Reagent Grade benzene and acetic acid were further purified for use. Each was fractionally recrystallized by allowing about one-half the starting volume to freeze, pouring off the liquid portion, and retaining the frozen material. Especial care was taken to avoid any exposure to other than dry air during all operations. The crystallization procedure was repeated to a total of three times, following the change in refractive index at each step. After the second crystallization, in the case of each solvent, no further change in $n^{25}D$ was observed. The final value of $n^{25}D$ was benzene 1.49806; acetic acid 1.36965. These values check those obtained by previous workers.[9,10] The densities (Table II) of the purified materials were also in close agreement with published results.[11]

Apparatus and Procedure.—The apparatus and procedure for the precision density measurements have been reported previously.[1] The only modification used in this work was to dry all glass equipment thoroughly with a $CaSO_4$-dried (Drierite) air stream to remove adsorbed water, and to equip all vents with $CaSO_4$ drying-tubes. The solutions for density determinations were prepared by weighing the individual components and the final compositions were calculated.

The kinematic viscosities were measured with a Cannon-Ubbelohde viscometer, whose calibration and use have been described earlier.[3] The solutions for viscosity determination were prepared by volume, and a sample was withdrawn from the efflux bulb of the viscometer after each run for analysis by refractive index. The concentration of the sample was read from a standard curve of refractive index *vs.* concentration; an accuracy of ±0.05 mole % was possible.

Refractive index measurements were made using a Bausch and Lomb precision refractometer capable of giving results accurate to ±0.00003 unit.

Results

Table I gives the kinematic-viscosity values for benzene–acetic acid solutions. The technique for the measurement is capable of giving results with an accuracy of ±0.1%. Every effort was made to maintain this accuracy, although the possibility exists that trace amounts of water, which may have been introduced through brief exposure to ordinary air during the viscosity runs, might have caused minor variations. Compared to the data of Table I, the results of Dunstan[5] average 5% high in the 0 to 60 mole % region; for the high-benzene region the agreement is within about ±1%. The results of Muchin[7] average 3% higher than those found here.

Table II gives the density values for benzene–acetic acid solutions. With the technique used, the possibility of trace water contamination is very remote, and the results are believed to have a maximum deviation of ±0.00005 g./ml. from the true value. The values reported by Hubbard[6] check the results of Table II within 0.0002 g./ml.;

(1) K. T. Thomas and R. A. McAllister, *A.I.Ch.E. Journal*, **3**, 161 (1957).

(2) K. S. Howard and R. A. McAllister, *ibid.*, **4**, in press (1958).

(3) K. S. Howard and R. A. McAllister, *ibid.*, **3**, 325 (1957).

(4) L. W. Hammond, K. S. Howard and R. A. McAllister, This Journal, **62**, 637 (1958).

(5) A. E. Dunstan, *J. Chem. Soc.*, **87**, 11 (1905).

(6) J. C. Hubbard, *Phys. Rev.*, **30**, 759 (1910).

(7) G. Muchin, *Z. Elektrochem.*, **19**, 819 (1913).

(8) P. B. Ganguly and S. K. Chakrabertty, *Z. anorg. allgem. Chem.*, **231**, 304 (1937).

(9) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publ. Co., Inc., New York, N. Y., 1950, p. 147. Benzene (av. 8), 1.49600.

(10) (a) R. R. Dreisbach, "Physical Properties of Chemical Compounds," American Chemical Society, Washington, D. C., 1955, p. 11. Benzene, 1.49792. (b) R. R. Dreisbach, "Physical Properties of Chemical Substances," Dept. Tech. Service and Develop., The Dow Chemical Co., Midland, Mich. Acetic acid, 1.36965.

(11) Timmermans (ref. 10) reports average densities of 0.87898 and 0.87367 g./ml. for benzene at 20 and 25°, respectively, and 1.04924 g./ml. for acetic acid at 20° Dreisbach reports 0.87901 and 0.87370 g./ml. for benzene (ref. 10a) at 20 and 25°, respectively, and 1.04923 g./ml. for acetic acid (ref. 10b) at 20°.

TABLE I

KINEMATIC VISCOSITY OF LIQUID BENZENE–ACETIC ACID SOLUTIONS

Mole % benzene	ν, cs.	Mole % benzene	ν, cs.
20.00°		25.00°	
0.0	1.1712	0.0	1.0888
3.1	1.0918	3.1	1.0332
9.3	0.9806	9.3	0.9146
17.6	.8794	17.5	.8268
25.2	.8170	25.1	.7668
36.9	.7568	55.1	.6712
43.1	.7366	64.1	.6650
55.2	.7153	79.5	.6670
63.8	.7133	89.9	.6763
79.5	.7125	100.0	.6915
89.9	.7231		
100.0	.7397		
37.80°		50.05°	
0.0	0.9117	0.0	0.7857
3.2	.8578	3.0	.7437
9.9	.7730	9.9	.6728
17.0	.7100	16.8	.6227
23.9	.6690	23.9	.5840
35.6	.6159	35.6	.5415
42.1	.6002	42.2	.5263
53.2	.5848	53.3	.5097
64.0	.5726	64.6	.5036
79.5	.5718	79.4	.5020
89.8	.5804	94.6	.5123
100.0	.5903	100.0	.5153
60.11°		70.20°	
0.0	0.7014	0.0	0.6320
3.1	.6671	3.7	.5959
9.3	.6099	9.3	.5542
17.5	.5578	17.0	.5118
25.3	.5242	23.9	.4827
36.8	.4884	36.8	.4471
43.3	.4765	43.2	.4358
55.1	.4616	54.95	.4225
63.85	.4571	63.8	.4169
79.5	.4548	79.5	.4156
90.0	.4587	89.9	.4182
100.0	.4658	100.0	.4253
80.35°		90.54°	
0.0	0.5732	0.0	0.5227
3.0	.5479	2.9	.5002
9.8	.5026	9.4	.4616
17.0	.4674	16.7	.4309
23.8	.4429	23.2	.4099
35.5	.4128		
42.9	.4020		
52.9	.3893		
64.4	.3826		
79.4	.3815		
89.9	.3820		

those of Muchin[7] are about 0.3% higher than those found here.

From the data of Tables I and II, the viscosities and densities at the normal boiling point were extrapolated, and are presented in Table III.

TABLE II

DENSITY OF LIQUID BENZENE–ACETIC ACID SOLUTIONS

Mole % benzene	ρ, g./ml.	Mole % benzene	ρ, g./ml.
20.00°		25.00°	
0.00	1.04928	0.00	1.04378
10.94	1.01570	21.82	0.98242
14.75	1.00549	40.49	.94512
28.96	0.97256	60.56	.91477
36.87	.95729	79.60	.89248
49.72	.93572	100.00	.87372
62.51	.91477		
78.28	.89929		
100.00	.87908		
37.80°		50.05°	
0.00	1.02934	0.00	1.01548
24.42	0.96212	10.94	0.98162
38.49	.93416	14.75	.97126
56.62	.90579	28.96	.93839
81.41	.87654	36.87	.92316
100.00	.85998	49.72	.90190
		62.51	.88426
60.11°		78.28	.86630
0.00	1.00400	100.00	.84667
21.82	0.94248	70.20°	
40.49	.90529	0.00	0.99242
60.56	.87539	24.42	.92499
79.60	.85357	38.49	.89697
100.00	.83564	56.62	.86903
80.35°		81.41	.84057
0.00	0.98081	100.00	.82456
12.78	.94144	90.54°	
30.06	.90083	0.00	0.96832
41.41	.87989	8.30	.94221
57.45	.85604	20.09	.91095

TABLE III

VISCOSITY AND DENSITY OF LIQUID BENZENE–ACETIC ACID SOLUTIONS AT THEIR NORMAL BOILING POINTS

Mole % benzene	B.p.,[a] °C.	ν, cs.	ρ, g./ml.	η, cp.
0	118.5	0.407	0.9353	0.381
10	106.1	.402	.9180	.369
20	98.8	.392	.9011	.353
30	93.9	.381	.8849	.337
40	90.4	.373	.8706	.325
50	87.7	.370	.8581	.317
60	85.6	.368	.8465	.312
70	83.8	.371	.8364	.310
80	82.4	.375	.8281	.311
90	81.2	.379	.8206	.311
100	80.1	.392	.8136	.319

[a] Boiling points of solutions from M. A. Rosanoff and C. W. Easeley, *J. Am. Chem. Soc.*, 31, 985 (1909). Boiling points of pure solvents from Timmermans, ref. 9.

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