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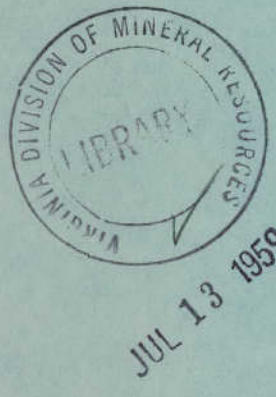

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VISCOSITIES AND DENSITIES OF METHANOL–TOLUENE SOLUTIONS UP TO THEIR NORMAL BOILING POINTS

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In a study of the effect of physical properties on the efficiency of distillation for the binary methanol–toluene system, the density, viscosity, molecular diffusivity and surface tension were needed at the boiling temperatures. The viscosity and density of methanol–toluene mixtures at 20° have been reported previously,[2,3] but it would not be possible to predict the boiling point values from these limited data, and therefore the present investigation was undertaken.

Experimental

Materials.—The methanol used was Baker Analyzed Reagent Grade. It was dried by heating just below the boiling point for 48 hr. over $CaSO_4$ which had been regenerated by drying at 200° for 5 hr. The methanol was then slowly distilled into a dry distilling receiver which was vented to the atmosphere through a $CaSO_4$ gas drying unit. The first and last fractions (each approximately $^1/_{10}$ of the original volume) of methanol were discarded and the middle cut of the distillate was retained. The methanol thus dried had a density at 20° of 0.7913 g./ml., which was in good agreement with accepted values.[4]

The toluene used was Baker Analyzed Reagent Grade, Lot. No. 1361. This lot was selected after careful investigation of the physical properties of many samples from different manufacturers. Several samples were purified by distillation and/or dried using a variety of desiccants, and their properties were examined. No sample of higher purity was obtained than this particular lot, which had a stated boiling range of 0.1°, an average $n^{25}D$ of 1.49405, and a density at 20° of 0.8669 g./ml.[5] The effect of trace water contamination of the toluene and methanol–toluene mixtures is described below.

Apparatus and Procedure.—The apparatus and procedure for the precision density measurements have been reported previously.[6] For mixtures having a methanol content of 25 mole % or less, it was extremely difficult to fill the pycnometer without having liquid droplets form on the capillary arms above the main liquid body. Recleaning the pycnometer, redistilling the solvents, filtering the solutions, and overnight soaking of the pycnometer in the solutions before the determination, all seemed to be of no avail in combatting the problem. As many as a dozen separate fillings of the pycnometer, on separate days, were often required before a successful determination could be made. No such trouble was encountered for pure methanol, for pure toluene, or for methanol compositions greater than 25 mole %.

Kinematic viscosities of the methanol–toluene solutions were measured in a Cannon–Ubbelohde viscometer. The technique of operation and the details of the calibrations have been reported previously.[7]

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

Results

The refractive index–composition values are in Table I. From these data a curve was drawn, from which was read the concentrations of samples drawn from the efflux bulb of the Cannon–Ubbelohde viscometer. Such analyses had an accuracy of ±0.1 mole % methanol over the whole concentration range. The results in the high concentration range (>50 mole % methanol) are even more precise since the refractive index–composition curve has a greater slope in this range.

Table I

Refractive Index of Methanol-Toluene Solutions

Methanol, mole %	$n^{25}D$
0.00	1.49405
4.57	1.49097
10.10	1.48710
21.91	1.47776
30.39	1.47002
40.47	1.45941
47.06	1.45116
60.22	1.43250
69.86	1.41523
81.73	1.38827
90.08	1.36397
95.20	1.34602
100.00	off scale

Table II gives the kinematic–viscosity values for methanol–toluene solutions. The results show that the viscosity at a given temperature has first a minimum and then a maximum when plotted against mole fraction of methanol.

The density of methanol–toluene mixtures is given in Table III. To investigate the error introduced by trace water contamination, samples were handled as if they were being loaded into a pycnometer, but instead they were analyzed by a Karl–Fischer titration.[8] Addition of 0.01 wt. % water changed the density not more than +0.00003 g./ml. In no case was there more than 0.03 wt. % water in the samples reported here. The effect on the reported density values was less than 0.0001 g./ml. A few runs indicated that the trace amounts of water present did not change the viscosity, within the reported accuracy.

The density, kinematic viscosity and absolute viscosity of methanol–toluene solutions at their normal boiling points were extrapolated, and these data are presented in Table IV.

The procedure for measuring the density[6] is capable of giving density values accurate to ±0.00002 g./ml. and every effort was made to uphold this precision. The data of Table III, however, are listed to only four significant figures for two reasons. (1) The difficulty in obtaining a good measurement below 25 mole % methanol made these data questionable in the fifth decimal place, and (2) different bottles of the same lot (Baker Analyzed Lot No. 1361) of toluene showed differences in the fifth

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(2) B. Ya. Teitel'baum, T. H. Gormaloua and S. G. Ganelina. *Zhur. Obshchei Khim.*, **82**, pt. 20, 1422 (1950).

(3) N. Madsen, *Science*, **114**, 500 (1951).

(4) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., New York, N. Y., 1950, p. 304.

(5) (a) Timmermans (ref. 4, p. 152) gives $n^{25}D$ of 1.49405 and a density at 20° of 0.8669 g./ml. for toluene; (b) R. R. Dreisbach, "Physical Properties of Chemical Compounds," Am. Chem. Soc., Washington, D. C., 1955, p. 12, gives $n^{25}D$ of 1.49414 and a density at 20° of 0.8669 g./ml.

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

(7) Katherine S. Howard and R. A. McAllister, *ibid.*, in press.

(8) J. Mitchell, Jr., and D. M. Smith, "Application of the Karl Fischer Reagent to Quantitative Analyses Involving Water," Interscience Publ., Inc., New York, N. Y., 1948.

TABLE II

KINEMATIC VISCOSITY OF LIQUID METHANOL–TOLUENE SOLUTIONS

Methanol, mole %	ν (centistoke)	Methanol, mole %	ν (centistoke)
20.00°		25.00°	
0.0	0.6786	0.0	0.6414
7.1	.6672	1.9	.6348
14.0	.6683	8.2	.6284
20.9	.6738	11.0	.6275
29.1	.6849	18.9	.6314
35.4	.6914	28.7	.6410
47.9	.7134	38.7	.6543
50.6	.7176	49.8	.6703
60.95	.7338	61.1	.6852
73.6	.7486	73.4	.7009
77.8	.7528	82.2	.7040
83.7	.7542	83.3	.7049
90.1	.7524	90.1	.7025
93.8	.7471	95.0	.6991
100.0	.7373	100.0	.6914
37.80°		50.05°	
0.0	0.5621	0.0	0.5009
3.1	.5533	2.8	.4938
9.1	.5480	8.9	.4876
13.6	.5482	15.0	.4852
19.2	.5487	19.8	.4845
29.1	.5542	25.8	.4865
46.3	.5700	34.0	.4887
60.6	.5829	42.5	.4938
68.8	.5904	60.3	.5056
71.15	.5931	68.7	.5103
77.8	.5959	79.4	.5152
84.0	.5982	89.8	.5163
90.45	.5977	100.0	.5138
100.0	.5908		
60.11°		70.20°	
0.0	0.4592	0.0	0.4238
2.6	.4530	4.65	.4125
8.8	.4454	9.75	.4086
19.6	.4410	80.35°	
26.3	.4404		
33.3	.4426	0.0	0.3922
41.4	.4455	4.92	.3839
52.9	.4499		
59.9	.4537		
68.4	.4575		
76.6	.4601		
80.9	.4610		
89.75	.4621		
100.0	.4590		

decimal place for both density and refractive index. It is assumed that these differences resulted from unknown amounts of dissolved water and possibly dissolved gases.

The procedure for measuring the viscosity resulted in viscosity data accurate to ±0.2%. The viscosity values given in Table IV are reported to three significant figures only because the boiling temperatures are no more accurate than 0.1°.

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TABLE III

DENSITY OF LIQUID METHANOL–TOLUENE SOLUTIONS

Methanol, mole %	ρ (g./ml.)	Methanol, mole %	ρ (g./ml.)
20.00°		50.05°	
0.00	0.8669	0.00	0.8389
24.82	.8589	24.22	.8302
49.55	.8470	49.37	.8181
76.13	.8267	76.38	.7972
100.00	.7913	100.00	.7630
25.00°		60.11°	
0.00	0.8622	0.00	0.8291
23.16	.8548	25.03	.8205
50.29	.8420	50.69	.8077
76.07	.8220	75.73	.7878
100.00	.7865	100.00	.7531
37.80°		70.20°	
0.00	0.8503	0.00	0.8193
10.62	.8469	10.04	.8163
24.64	.8422	80.35°	
37.53	.8364	0.00	0.8097
49.84	.8299	5.95	.8078
65.53	.8193		
76.13	.8096	90.54°	
87.34	.7962	0.00	0.7995
95.47	.7834		
100.00	.7746		

TABLE IV

DENSITY AND VISCOSITY OF LIQUID METHANOL–TOLUENE SOLUTIONS AT THEIR NORMAL BOILING POINTS

Methanol, mole %	B.p.[a] (°C.)	ρ (g./ml.)	ν (cs.)	η (cp.)
0	110.7	0.7801	0.329	0.257
5	83.5	.8041	.376	.302
10	74.0	.8155	.396	.323
15	69.2	.8149	.409	.333
20	67.6	.8147	.413	.336
25	66.7	.8140	.415	.338
30	66.2	.8126	.417	.339
35	65.8	.8109	.419	.340
40	65.5	.8088	.421	.341
45	65.2	.8061	.424	.342
50	65.0	.8035	.427	.343
55	64.7	.8001	.431	.345
60	64.5	.7966	.435	.347
65	64.3	.7928	.438	.347
70	64.1	.7891	.440	.347
75	63.9	.7853	.442	.347
80	63.8	.7799	.444	.346
85	63.7	.7734	.445	.344
90	63.5	.7681	.446	.343
95	63.7	.7595	.444	.337
100	64.5	.7488	.438	.328

[a] Boiling points of the solutions from the data of M. Benedict, C. L. Johnson, E. Solomon and L. C. Rubin, *Trans. Am. Inst. Chem. Engrs.*, **41**, 3171 (1945). Boiling points of the pure components from Timmermans (ref. 4) and Dreisbach (ref. 5).