Part II

PHYSICAL PROPERTIES

EVALUATION OF COMPOUNDS AND MATERIALS

Viscosities and Densities of Acetone-Benzene and Acetone–Acetic Acid Systems up to Their Normal Boiling Points

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In a study of the effect of physical properties on the contact efficiency of distillation, various properties of selected binary liquid systems have been measured in these laboratories over a wide temperature range, and extrapolated to the boiling points. Properties of the acetone-water system (*8, 9, 15*), the methanol-toluene system (*6*), and the benzene–acetic acid system (*7*) have been reported. Two more acetone systems were of interest in the distillation study, one with benzene as the second component, and one with acetic acid. A few measurements of the viscosity and density of the acetone-benzene system at 20° and 25° C were reported (*1, 2, 4, 13*), but the properties at the boiling points of the solutions could not be estimated from these limited values. For acetone–acetic acid, again only a few scattered measurements could be located (*3,11,12,17*).

REAGENTS

Baker analyzed reagent grade (J. T. Baker Co., Phillipsburg, N. J.) benzene, acetone, and acetic acid were further purified for use. The purification procedures and the comparisons of the properties of the final products with reported values have been given (*7, 10*). In both cases, the properties of the final products were in close accord with those reported for very pure materials.

Acetone-Benzene System

EXPERIMENTAL

The modified Robertson pycnometers and the procedure for the precision density measurements have been described (*15*). The only modifications used here involved drying all glass surfaces prior to use with a calcium sulfate–dried (Drierite) air stream to remove adsorbed water, and equipping all vents with calcium sulfate drying tubes to avoid any exposure to moist air. The solutions were prepared by weighing the individual components and the final concentrations were calculated, reducing all weights to the in vacuo values.

The kinematic viscosities were measured using Cannon-Ubbelohde viscometers; their calibration and used has been reported (*9*). Solutions were prepared by volume, and the refractive indices (n_D^{25}) of samples withdrawn after each run from the viscometer efflux bulb were measured. The exact solution concentration was then determined by reference to a standard curve of n_D^{25} *vs.* concentration. An accuracy to ±0.05 mole % was possible.

The refractive index was measured using a Bausch and Lomb precision refractometer with a reproducibility to ±0.00003 unit.

RESULTS

Table I gives the measured density values for the acetone-benzene system. With the precautions used, the possibility of trace water contamination was remote, and the results were precise to ±0.00005 gram per ml. The literature values (*1, 2, 4, 13*) are within ±0.5% of these values and are generally high. This deviation is probably due to the failure of these workers to have anhydrous acetone.

The kinematic viscosity values for the system are given in Table II. The technique used for measurement is capable of an accuracy to ±0.1%, but it is doubtful whether this accuracy was maintained except in the region 0 to 25 mole % acetone, and for 100% acetone. The viscosities were measured before the procedure for acetone desiccation had been successfully completed, and the "100% acetone" used to prepare the acetone-benzene solutions actually contained up to 0.2 mole % water. In a supplementary study the effect of water contamination on the viscosity of acetone-benzene solutions was determined. At low acetone concentration (6.0 mole %), the addition of water up to saturation caused no detectable change (<0.1%) in the viscosity; at high acetone concentration (95 mole %), where larger amounts of water were soluble, viscosity was increased upon successive additions of water. From this study it was con-

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Table I. Densities of Liquid Acetone-Benzene Solutions

Mole % Acetone	ρ, G./Ml.	Mole % Acetone	ρ, G./Ml.	Mole % Acetone	ρ, G./Ml.
20.00° C.		37.80° C.		60.11° C.	
0.00	0.87908	0.00	0.85998	0.00	0.83564
15.46	0.86760	9.35	0.85303	15.97	0.82365
30.71	0.85574	26.83	0.83966	29.36	0.81278
44.34	0.84435	39.46	0.82918	39.20	0.80437
55.05	0.83488	57.17	0.81344	49.76	0.79495
63.46	0.82715	72.55	0.79857		
71.20	0.81970	83.32	0.78758	70.20° C.	
82.28	0.80869	100.00	0.76944		
100.00	0.78994			0.00	0.82456
				4.42	0.82117
25.00° C.		50.05° C.		9.35	0.81737
0.00	0.87372	0.00	0.84667		
15.97	0.86200	15.46	0.83509		
29.36	0.85145	30.71	0.82293		
39.20	0.84334	44.34	0.81125		
49.76	0.83416	55.05	0.80157		
57.17	0.82756	63.46	0.79357		
72.55	0.81290	71.20	0.78601		
83.32	0.80205	82.28	0.77448		
100.00	0.78425	100.00	0.75482		

Table II. Kinematic Viscosities of Liquid Acetone-Benzene Solutions[a]

Mole % Acetone	ν, Cs.	Mole % Acetone	ν, Cs.	Mole % Acetone	ν, Cs.
20.00° C.		25.00° C.		50.05° C.	
0.0	0.7397	0.0	0.6915	0.0	0.5153
6.0	0.705	6.0	0.661	16.0	0.470
16.2	0.654	16.1	0.614	16.2	0.470
17.65	0.647	17.55	0.608	27.4	0.442
28.6	0.599	28.6	0.566	39.8	0.414
39.1	0.559	39.1	0.529	50.3	0.394
39.2	0.557	50.25	0.495	58.4	0.379
50.3	0.520	69.1	0.444	69.3	0.360
59.3	0.492	78.2	0.424	78.25	0.346
69.0	0.465	87.0	0.406	87.0	0.334
78.3	0.443	100.0	0.3846	95.5	0.324
87.1	0.423			100.0	0.3193
95.6	0.408	37.80° C.			
100.0	0.4004			60.11° C.	
		0.0	0.5903		
		5.9	0.568	0.0	0.4658
		16.1	0.533	16.1	0.427
		17.4	0.528	27.4	0.405
		28.55	0.494	39.7	0.381
		38.7	0.466	50.2	0.363
		59.1	0.418	58.3	0.351
		69.0	0.398		
		78.2	0.381	70.20° C.	
		87.0	0.367		
		100.0	0.3481	0.0	0.4253

[a]Error due to water contamination increases with increasing acetone concentration.

cluded that these reported viscosities for acetone-benzene solutions may be 0.2 to 0.3% high in the region of 30 to 60 mole % acetone, and from 0.4 to a maximum of 0.6% high in the region of 65 to 99 mole % acetone. The values listed for 100% acetone are correct for properly desiccated material.

The literature values (*3, 11, 12, 17*) for the viscosity of acetone-benzene do not agree with those reported here to better than 1 to 3%. In general, the reported values in the high acetone region are even higher than those found here, possibly indicating the presence of even more water contamination.

From the data of Tables I and II, the densities and viscosities at the normal boiling points were extrapolated; these values are given in Table III. For the extrapolation, plots were first made

Table III. Viscosities and Densities of Liquid Acetone-Benzene Solutions at Their Normal Boiling Points[a]

Mole % Acetone	B.P.,[b] °C.	ν, Cs.	ρ, G./Ml.	η, Cp.
0	80.1	0.392	0.8136	0.319
10	74.0	0.390	0.8124	0.317
20	70.0	0.385	0.8094	0.312
30	66.8	0.378	0.8048	0.304
40	64.2	0.369	0.7991	0.295
50	62.2	0.358	0.7924	0.284
60	60.7	0.347	0.7848	0.272
70	59.4	0.336	0.7764	0.261
80	58.2	0.324	0.7673	0.249
90	57.1	0.314	0.7576	0.238
100	56.2	0.308	0.7473	0.230

[a]Extrapolated from the experimental data of Tables I and II.
[b]Boiling points of pure solvents from (*16*), of solutions, smoothed data of Gerster (*5*) and Ebersole (*2*).

of density and viscosity against mole per cent acetone on rectangular coordinates. From these smooth curves, cross plots were made of density and viscosity against temperature for constant mole per cent of acetone, again on regular coordinates. These final lines were only slightly curved, hence were suitable for extrapolation, particularly because the average extrapolation from the data was only 6° C.

Acetone–Acetic Acid System

EXPERIMENTAL

The apparatus and techniques for determination of density, viscosity, and refractive index were the same as for acetone-benzene. For most of the viscosity samples, the refractive index (n_D^{25}) was measured, and the concentration was determined by reference to a standard curve of refractive index *vs.* concentration. An accuracy to ±0.2 mole % was possible. In the low-acetone region (up to 20 mole % acetone), refractive index was unsuitable for analysis, for the standard curve had a maximum

Table IV. Densities of Liquid Acetone–Acetic Acid Solutions

Mole % Acetone	ρ, G./Ml.	Mole % Acetone	ρ, G./Ml.	Mole % Acetone	ρ, G./Ml.
20.00° C.		37.80° C.		60.11° C.	
0.00	1.04928	0.00	1.02934	0.00	1.00400
15.15	1.00679	10.56	0.99948	15.11	0.96130
23.32	0.98425	23.17	0.96477	25.09	0.93376
39.19	0.94147	37.60	0.92565	39.92	0.89380
52.05	0.90776	54.24	0.88225	55.15	0.85403
54.38	0.90186	65.94	0.85258	65.71	0.82741
55.42	0.89913	73.37	0.83427	75.30	0.80359
62.29	0.88177	87.81	0.79895		
77.36	0.84447	100.00	0.76944	70.20° C.	
90.18	0.81355				
100.00	0.78994	50.05° C.		0.00	0.99242
				15.11	0.94971
25.00° C.		0.00	1.01548	25.09	0.92242
		15.15	0.97285	39.92	0.88221
0.00	1.04378	23.32	0.95025	55.15	0.84249
10.56	1.01390	39.19	0.90748		
23.17	0.97910	52.05	0.87369	80.35° C.	
37.60	0.93999	54.38	0.86779		
54.24	0.89659	55.42	0.86508	0.00	0.98081
65.94	0.86701	62.29	0.84763	12.05	0.94638
73.37	0.84863	77.36	0.81013	25.58	0.90883
87.81	0.81355	90.18	0.77881	32.35	0.89064
100.00	0.78425	100.00	0.75482		
				90.54° C.	
				0.00	0.96833
				7.92	0.94601
				20.55	0.91080

at 10 mole %. For this region, the samples were diluted with water and titrated with sodium hydroxide to a phenolphthalein end point. This analysis was of a comparable order of accuracy.

RESULTS

The density values for the acetone–acetic acid system are given in Table IV. For this system also, the possibility of water contamination was remote and the reproducibility of duplicate determinations was well within ±0.00005 gram per ml. The literature values (*11*, *17*) are within ±0.4% of these results, and the deviation is random. In both these reported cases, the acetone was apparently contaminated by a higher-density material, probably water.

The kinematic viscosity values for the system are listed in Table V. Although the technique used for the determinations is capable of an accuracy of ±0.1%, this accuracy could not be maintained, owing mainly to limitations in the refractive index analytical technique. In addition, the viscosities were measured before the acetone desiccation procedure had been successfully carried out, and the acetone used to prepare the acetone–acetic acid solutions contained up to 0.2 mole % water. This amount of water contaminant would have been undetectable for solutions up to an acetone concentration of about 50 mole %, but the reported values may be higher (up to +0.5%) than the true values in the high-acetone region. Hence, the accuracy of the viscosities of the acetone–acetic acid solutions cannot be considered better than ±1.0%; the values for 100% acetone and acetic acid, however, are probably within ±0.1%.

Table V. Kinematic Viscosities of Liquid Acetone-Acetic Acid Solutions[a]

Mole % Acetone	ν, Cs.	Mole % Acetone	ν, Cs.	Mole % Acetone	ν, Cs.
20.00° C.		37.80° C.		60.11° C.	
0.0	1.1712	0.0	0.9117	0.0	0.7014
4.4[b]	1.150	4.4[b]	0.897	4.5[b]	0.689
12.8[b]	1.078	12.4[b]	0.845	12.1[b]	0.653
21.2	0.985	20.3	0.785	20.4	0.615
29.3	0.901	29.1	0.722	25.1	0.596
38.1	0.812	38.7	0.654	38.7	0.527
51.1	0.701	39.5	0.654	43.7	0.508
57.7	0.647	48.7	0.595	48.5	0.483
70.1	0.564	59.5	0.531	58.0	0.439
81.2	0.497	69.7	0.477	59.2	0.438
92.6	0.436	81.7	0.423	69.9	0.395
100.0	0.4004	93.4	0.375		
		100.0	0.3481	70.20° C.	
25.00° C.				0.0	0.6320
		50.05° C.		4.6[b]	0.620
0.0	1.0888			13.0[b]	0.590
4.3[b]	1.068	0.0	0.7857	21.3	0.552
13.2[b]	1.004	4.1[b]	0.771	28.7	0.519
21.2	0.922	12.5[b]	0.728	37.7	0.479
28.7	0.845	21.2	0.680	40.8	0.472
38.5	0.764	29.7	0.629	49.2	0.441
48.2	0.683	38.7	0.575	50.7	0.431
57.8	0.618	43.1	0.554		
69.8	0.536	48.3	0.532	80.35° C.	
81.3	0.475	51.4	0.515		
92.1	0.419	58.0	0.483	0.0	0.5732
100.0	0.3846	59.5	0.478	5.3[b]	0.566
		70.0	0.426	12.3[b]	0.536
		81.5	0.384	20.8	0.504
		92.7	0.343	29.1	0.472
		100.0	0.3193	38.6	0.439
				90.54° C.	
				0.0	0.5227
				5.0[b]	0.513
				13.1[b]	0.489
				22.5	0.462

[a] Error due to water contamination increases with increasing acetone concentration.
[b] Analysis by titration, remaining solutions analyzed by refractive index.

Table VI. Viscosities and Densities of Liquid Acetone–Acetic Acid Solutions at Their Normal Boiling Points[a]

Mole % Acetone	B.P.,[b] °C.	ν, Cs.	ρ, G./Ml.	η, Cps.
0	118.5	0.407	0.9353	0.381
10	103.2	0.451	0.9254	0.417
20	93.1	0.462	0.9092	0.420
30	85.8	0.449	0.8906	0.400
40	79.7	0.436	0.8711	0.380
50	74.6	0.420	0.8504	0.357
60	70.0	0.401	0.8303	0.333
70	66.1	0.379	0.8096	0.307
80	62.6	0.354	0.7891	0.279
90	59.2	0.330	0.7685	0.254
100	56.2	0.308	0.7473	0.230

[a] Extrapolated from data of Tables IV and V.
[b] Boiling points of pure solvents from (*16*), of solutions, smoothed data of Othmer (*14*). These data are not entirely consistent with values reported by York and Holmes (*18*). Accuracy of the b.p. data cannot be evaluated, so no estimate of the accuracy of extrapolated values is possible. Should additional b.p. information become available, extrapolation could be repeated to obtain density and viscosity values of comparable accuracy.

The viscosity values reported by other workers (*11*, *17*) average within about ±1.0% of those reported here, the exceptions being the values reported for "100%" acetone and acetic acid, where the deviations are larger. In the latter cases, the deviations could be explained by the presence of water as a contaminant.

From the data of Tables IV and V, the densities and viscosities at the normal boiling points were extrapolated (Table VI). The extrapolation procedure was the same as for acetone-benzene. The average extrapolation required for both density and viscosity was 8° C.

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