

at this temperature. Table II gives a comparison of the average data.

Viscosity values for air for intermediate temperatures were calculated by Sutherland's equation (9).

The relative viscosities of the vapors with respect to air were calculated by means of Equation 19. The absolute viscosities of the vapors were then calculated using the viscosity values of air determined by means of the Sutherland equation.

EXPERIMENTAL DATA

Experimental vapor viscosity data for the 1-propanol-water system were determined at 110°, 130°, and 150°C. and for the *n*-octane-toluene system at 130° and 150°C. (Table III).

ACKNOWLEDGMENT

The authors wish to express their sincere appreciation to the National Science Foundation for its aid in carrying out this and related investigations.

LITERATURE CITED

- (1) Adam, N. K., "Physics and Chemistry of Surface," 3rd ed., Oxford University Press, London, 1944.
 - (2) Cottrell, F. G., *J. Am. Chem. Soc.* **41**, 721 (1919).
 - (3) Ferguson, A., Kennedy, S. J., *Proc. Phys. Soc.* **44**, 511 (1932).
 - (4) Hilsenrath, J., others, *Natl. Bur. Standards, Circ.* **564** (Nov. 1, 1955).
 - (5) Jackson, W. M., *J. Phys. Chem.* **60**, 789 (1956).
 - (6) Myerson, A. L., Eicher, J. H., *J. Am. Chem. Soc.* **74**, 2758 (1952).
 - (7) Poiseuille, J. L. M., *Compt. rend.* **11**, 961 (1840).
 - (8) Ruches, W., *Ann. Physik* **4**, 983 (1908).
 - (9) Sutherland, W., *Phil Mag.* **36**, 507 (1895).
- Received for review August 23, 1956. Accepted April 8, 1957.

Properties of Binary Mixtures as a Function of Composition

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Data on physical properties of mixtures as a function of composition and temperature are valuable in correlating other properties and in analytical studies. In this and subsequent investigations an attempt was made to develop experimental data for a number of systems on which generalized correlations could be developed relating composition and the property evaluated based on the properties of the pure components. Thus, eight binary systems having a rather wide range of properties (particularly interfacial tension) and in most cases, representing nonideal liquid mixtures were studied. The systems were: 1-propanol-water; toluene-*n*-octane; water-1-butanol; acetone-1-butanol; benzene-2-chloroethanol; carbon tetrachloride-1-propanol; ethyl alcohol-1,4-dioxane; and methanol-1,4-dioxane. The properties determined were: refractive index vs. composition, liquid density vs. composition and temperature, interfacial tension at the boiling point and at 30°C. as a function of composition, liquid viscosity as a function of temperature and composition, and vapor viscosity as a function of temperature and composition. Because of the peculiar variation of interfacial tension and viscosity with composition at the boiling point, no general correlations have been developed. More data on both binary and ternary systems are necessary.

MATERIALS

All the chemicals used for this project except toluene and water were reagent grade chemicals. Nitration grade toluene was used. Water was purified by distillation in this laboratory to a maximum conductivity of 1.4×10^{-6} mho or less. The refractive index of the materials was measured and compared with the reported values in the literature. They are listed in Table I.

REFRACTIVE INDEX

Refractive index vs. composition data for each binary system were obtained in the following manner.

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Table I. Refractive Index of Material Used

Material	Temp., °C.	Literature	Exptl.
Acetone	20.0	1.35911 (18)	1.35860
	25.0	1.35662 (18)	1.35625
Benzene	20.0	1.5011 (9)	1.50116
	25.0	1.49790 (18)	1.49733
	30.0	1.49486 (18)	1.49459
1-Butanol	20.0		1.39919
	25.0	1.3970 (18)	
	30.0	1.3974 (18)	1.39739 1.39538
Carbon tetrachloride	20.0	1.4602 (18)	1.46014
		1.46026 (18)	
		1.46036 (18)	
		1.46023 (18)	
	25.0	1.45732 (18) 1.4576 (18)	1.45740
2-Chloroethanol	20.0	1.44208 (18)	1.44198
	25.0		1.43977
1,4-Dioxane	20.0	1.4224 (9)	1.42223
	25.0	1.42025 (18)	
		1.4202 (18)	1.41973
		1.4202 (18)	
Ethyl alcohol	20.0	1.36139 (18)	1.36132
	25.0	1.3596 (18)	
		1.3595 (18)	
		1.359408 (18)	1.35937
Methanol	15.0	1.33057 (18)	1.33065
	20.0		1.32895
	25.0		1.32707
<i>n</i> -Octane	20.0		1.39775
	25.0	1.39534 (18)	
		1.39530 (18)	
		1.39509 (18)	
		1.39505 (18)	1.39564 1.39303
30.0			
1-Propanol	20.0	1.3854 (9)	1.38572
	23.6	1.3840 (18)	1.38452
	25.0		1.38391
	30.0		1.38183
Toluene	20.0	1.49682 (18)	1.49680
	25.0	1.49405 (18)	1.49407
	30.0		1.49134
Water	20.0	1.33300 (10)	1.33316
	25.0	1.33255 (14)	1.33277
	30.0	1.3320 (10)	1.33213

Table II. Refractive Index of Binary Mixtures

1-Propanol-Water		Toluene-n-Octane		Water-1-Butanol		Acetone-1-Butanol	
Mole % 1-propanol	n_D^{30}	Mole % toluene	n_D^{30}	Mole % water	n_D^{30}	Mole % acetone	n_D^{30}
At 30 °C.							
0.00	1.33213	0	1.39303	0	1.39538	0	1.39739
2.79	1.34000	2.785	1.39470	6.165	1.39488	6.634	1.39520
3.37	1.34160	13.26	1.40138	10.59	1.39444	19.20	1.39063
5.06	1.34568	28.29	1.41206	16.48	1.39377	26.37	1.38810
7.96	1.35113	43.40	1.42438	21.45	1.39312	29.89	1.38679
10.68	1.35494	43.89	1.42484	24.04	1.39271	38.43	1.38346
15.52	1.36025	50.00	1.43035	27.41	1.39217	48.45	1.37943
20.12	1.36414	51.53	1.43176	36.58	1.39052	50.00	1.37882
25.17	1.36756	54.36	1.43437	39.98	1.38976	55.89	1.37650
33.15	1.37160	65.74	1.44611	40.47	1.38959	63.58	1.37333
46.22	1.37600	83.38	1.46719	Two liquid phases		68.82	1.37114
50.00	1.37677	93.82	1.48179	98.72	1.33724	81.87	1.36500
54.98	1.37795	100.0	1.49134	99.50	1.33412	91.52	1.36041
64.25	1.37956			100.00	1.33213	92.53	1.34997
73.19	1.38060					97.17	1.35766
81.65	1.38140					100.0	1.35625
83.72	1.38159						
93.31	1.38180						
96.38	1.38183						
100.0	1.38183						
At 25 °C.							
Benzene-Ethylene Chlorohydrin		Carbon Tetrachloride- 1-Propanol		Ethyl Alcohol-1,4-Dioxane		Methanol-1,4-Dioxane	
Mole % benzene	n_D^{25}	Mole % CCl ₄	n_D^{25}	Mole % ethyl alcohol	n_D^{25}	Mole % methanol	n_D^{25}
0.00	1.43977	0.00	1.38368	0.00	1.41973	0.00	1.41973
1.40	1.44088	4.91	1.38855	3.195	1.41837	3.367	1.41828
3.71	1.44254	14.92	1.34781	5.81	1.41729	8.77	1.41587
7.27	1.44516	20.34	1.40261	12.09	1.41455	16.50	1.41217
14.17	1.44990	33.55	1.41331	23.02	1.40961	29.45	1.40513
18.35	1.45268	43.39	1.42067	33.01	1.40469	38.31	1.39953
27.15	1.45821	50.33	1.42567	41.64	1.40013	51.78	1.38950
37.23	1.46438	60.70	1.43270	47.44	1.39690	56.27	1.38569
42.91	1.46773	69.04	1.43818	57.54	1.39097	66.09	1.37629
50.00	1.47163	80.28	1.44525	65.44	1.38594	72.26	1.36962
51.09	1.47222	85.64	1.44846	73.94	1.38016	80.37	1.35956
60.01	1.47700	91.84	1.45227	82.03	1.37425	85.39	1.35240
69.77	1.48200	95.25	1.45426	87.16	1.37021	92.96	1.34032
77.63	1.48599	98.01	1.45599	93.44	1.36507	95.21	1.33621
88.71	1.49136	100.0	1.45740	96.42	1.36249	97.80	1.33142
93.48	1.49373			98.53	1.36063	99.00	1.32905
97.28	1.49572			100.0	1.35937	100.0	1.32707
100.0	1.49733						

After the weighed mixture was prepared, a magnetic stirrer was used to mix the two components of each of the binary systems, to obtain a uniform composition of the mixture. If the mixing were accomplished by shaking, it might be possible for an indeterminable amount of the system of different composition to adhere to the ground joint of the weighing bottle. A small magnet was sealed in a glass tube and placed in a dry 30-ml. weighing bottle which was then weighed. A predetermined amount of the less volatile component of the system was measured into the weighing bottle with a pipet and the weighing bottle with its contents was again weighed before addition of a calculated amount of the more volatile component to the system. The weight of the bottle with both components of the system was then obtained. As soon as the last weighing was completed, the weighing bottle containing the mixture was placed on the magnetic stirrer for thorough mixing of the system.

The refractive index of the mixture was then measured at 25° or 30°C. in a Bausch & Lomb precision refractometer equipped with a sodium arc lamp. The precision of measurement is 0.00003 unit of refractive index. The compositions of the mixtures were calculated to 0.01 mole % of the more volatile component.

Thirteen to 20 refractive index vs. composition points were obtained for each system covering the single-liquid-phase composition range. A smooth curve was drawn

through the experimental data points so that random error could be detected. The refractive index-composition data are reported in Table II.

Discussion of Refractive Index-Composition Data. The refractive index-composition data for four of the eight systems reported are available in the literature. Amis, Choppin, and Padgett (1) give equations to calculate n_D^f for the methanol-1,4-dioxane system. Values of n_D^{25} for ethyl alcohol-1,4-dioxane are furnished by Hopkins, Yerger, and Lynch (8); and those for the acetone-1-butanol system by Brunjes and Furnas (4). Data for the carbon tetrachloride-1-propanol system n_D^{20} are listed by Carley and Bertelsen (6). The data resulting from this investigation agree fairly closely with the refractive index data for the dioxane systems reported in the literature. Those for carbon tetrachloride-1-propanol system have not been compared because the temperature of measurement was different. However, the end point values agree with the established values in the literature (18). The refractive index data for the acetone-1-butanol binary system obtained in this laboratory are consistently lower than those reported in the literature. The extent of variation in terms of temperature is approximately 2°C. Random data points were rechecked and the temperature-calibration was rerun. The same results were obtained.

LIQUID DENSITY

Apparatus. The apparatus used for the liquid density determination was the following: A weighing device utilizing the same principles as a Westphal specific gravity balance consisted of a Chainomatic specific gravity balance set above a temperature bath. A borosilicate glass plummet, 9.255 ml. in volume, was employed at 26.4°C. to displace liquid contained in a 38 × 200 mm. borosilicate glass test tube clamped in the temperature bath directly below the hole in the base of the balance case. The temperature of the bath was controlled by a Bronwill constant temperature circulator to 0.1°C. Distilled water was used in the bath for temperatures of 30° and 55°C. while water-white mineral oil was used for temperatures of 75°C. and higher.

A Bausch & Lomb precision refractometer was used to determine the refractive index of the samples at 30° or 25°C. in order to obtain their composition from calibration charts.

Experimental Procedure. The liquid density of each of the eight binary systems was determined for several compositions at 30°, 55°, 75°, and 95°C.

A sample of the solution was placed in a 38 × 200 mm. test tube to a level about 5 cm. from the top; a stopper wrapped with aluminum foil was used to plug the opening of the test tube. The tube and its contents were placed in the temperature bath for sufficient time to allow the temperature to become constant before the measurement of the density of the sample. After removal of the stopper, the borosilicate glass plummet was immediately placed in the liquid sample. Care was taken to ensure that the plummet was freely suspended in the liquid by a fine Nichrome wire, which connected the plummet to the arm of the balance. Sufficient time was allowed for the plummet and liquid to reach thermal equilibrium. The weight lost by the plummet and the immersed portion of the wire in the liquid was divided by the total immersed volume to give the density of the sample at the bath temperature.

Evaporation of the liquid samples at higher temperatures limited measurement of liquid densities by this method. Densities for several samples could not be determined at temperatures of 75° to 95°C.

Discussion of Liquid Density Data. Data on liquid density expressed as a function of liquid composition and temperatures of 30°, 55°, 75°, and 95°C. for each system are presented in Table III. The estimated precision in the liquid density determination was 0.05%.

It was observed that the mixture densities of some of the systems studied are additive volumetrically.

The 1-propanol-water system is nonadditive volumetrically. The liquid mixture becomes less nonideal as the temperature approaches the boiling point.

The density of the toluene-*n*-octane mixture is additive on a volume basis. This relation still holds fairly well at temperatures near the boiling point.

For the water-1-butanol system the density is linear with liquid volumetric composition up to 14 mole % or more water at temperatures close to the boiling point of the solution.

The liquid density of the acetone-1-butanol mixture is volume-additive at high acetone concentrations.

The liquid density for the benzene-2-chloroethanol mixture is fairly close to being volume-additive.

The liquid density for the carbon tetrachloride-1-propanol mixture is fairly close to being volume-additive.

The liquid density for the ethyl alcohol-1,4-dioxane mixture is fairly close to being volume-additive.

The liquid density for methanol-1,4-dioxane system is linear to volume composition up to 70 mole % of methanol in the liquid.

INTERFACIAL TENSION

Interfacial tension measurements were made on various liquid compositions of each of the eight binary systems at their respective atmospheric boiling points and in contact with their equilibrium vapors.

Table III. Liquid Density vs. Composition and Temperature

Compn., Mole %	Density, Gram/ML.			
	30°C.	55°C.	75°C.	95°C.
1-Propanol-Water				
1-Propanol				
0.00	0.9956	0.9857	0.9749	0.9619
2.45	0.9832	0.9721	0.9600	0.9471
7.60	0.9609	0.9453	0.9310	0.9162
50.80	0.8438	0.8252	0.8069	0.7890
57.73	0.8364	0.8151	0.7968	0.7777
79.70	0.8144	0.7928	0.7748	0.7536
100.00	0.7966	0.7761	0.7576	0.7394
Toluene- <i>n</i> -Octane				
Toluene				
0.00	0.6945	0.6743	0.6580	0.6427
26.34	0.7239	0.7138	0.6871	0.6709
41.84	0.7447	0.7243	0.7079	0.6907
82.82	0.8159	0.7942	0.7765	0.7595
86.37	0.8227	0.8016	0.7837	0.7660
88.80	0.8295	0.8076	0.7896	0.7727
94.17	0.8419	0.8196	0.8019	0.7844
100.00	0.8577	0.8347	0.8162	0.7980
Water-1-Butanol				
Water				
0.00	0.8020	0.7829	0.7670	0.7482
9.50	0.8091	0.7897	0.7718	0.7539
25.26	0.8177	0.7989	0.7822	0.7622
43.85	0.8348	0.8148	0.7978	0.7788
	(Two liquid phases)			
98.704	0.9870	0.9765	0.9654	0.9521
100.00	0.9956	0.9857	0.9749	0.9619
Acetone-1-Butanol				
Acetone				
0.00	0.8020	0.7829	0.7670	0.7482
11.52	0.8012	0.7803	0.7628	
14.47	0.8010	0.7801	0.7625	
46.85	0.7931	0.7691	0.7499	
70.32	0.7873	0.7618		
79.74	0.7849	0.7583		
100.00	0.7797	0.7509		
Benzene-Ethylene Chlorohydrin				
Benzene				
0.00	1.1912	1.1635	1.1405	1.1182
33.65	1.0635	1.0356	1.0138	0.9918
48.32	1.0137	0.9862	0.9647	
66.11	0.9605	0.9332	0.9111	
84.90	0.9076	0.8801	0.8583	
100.00	0.8685	0.8416	0.8192	
Carbon Tetrachloride-1-Propanol				
CCl ₄				
0.00	0.7966	0.7761	0.7576	0.7394
54.99	1.2359	1.2005	1.1678	
74.00	1.3983	1.3552	1.3198	
100.00	1.5725	1.5246	1.4867	
Ethyl Alcohol-1,4-Dioxane				
Ethyl Alcohol				
0.00	1.0225	0.9944	0.9718	0.9487
21.01	0.9854	0.9580	0.9355	0.9151
58.22	0.9098	0.8841	0.8641	
70.56	0.8736	0.8485	0.8292	
96.53	0.7922	0.7699	0.7518	
100.00	0.7805	0.7587	0.7410	
Methanol-1,4-Dioxane				
Methanol				
0.00	1.0225	0.9944	0.9718	0.9487
22.50	0.9943	0.9676	0.9466	
41.15	0.9648	0.9386	0.9187	
66.20	0.9033	0.8824		
92.30	0.8183	0.7947		
100.00	0.7818	0.7591		

Table IV. Interfacial Tension at Normal Boiling Point and 30°C.

Water-1-Butanol			Acetone-1-Butanol		
Mole % water	δ , dynes/cm.	$t^\circ\text{C}$.	Mole % acetone	δ , dynes/cm.	$t^\circ\text{C}$.
At Boiling Point					
0.00	14.14	117.8	0.00	14.15	117.8
7.45	14.63	107.6	4.31	15.90	110.0
17.25	15.34	101.2	8.90	16.50	103.5
31.26	16.11	96.2	24.45	17.11	87.2
48.05	17.08	93.7	39.61	17.38	76.2
99.30	46.05	96.1	72.16	17.43	64.0
99.68	53.10	97.3	100.0	17.50	56.11
100.0	58.85	100.0			
At 30°C.					
0.00	23.75		0.00	23.75	
9.50	24.20		11.52	23.69	
25.26	24.19		23.07	23.60	
43.85	24.14		33.41	23.53	
100.0	71.18		46.85	23.26	
			70.32	22.63	
			79.74	22.22	
			100.0	22.01	
Benzene-2-Chloroethanol			Carbon Tetrachloride-1-Propanol		
Mole % benzene	δ , dynes/cm.	$t^\circ\text{C}$.	Mole % CCl_4	δ , dynes/cm.	$t^\circ\text{C}$.
At Boiling Point					
0.00	24.17	128.6	0.00	15.78	97.19
5.04	23.94	98.8	4.95	16.88	91.3
19.00	23.71	88.1	15.91	18.35	83.1
34.97	23.29	84.6	33.34	19.28	76.8
45.13	23.05	83.5	61.81	19.73	74.0
58.57	22.57	82.4	75.37	20.05	73.5
75.10	21.98	81.3	98.06	20.46	75.4
84.50	21.62	80.7	100.00	20.79	76.75
94.85	20.98	80.2			
100.00	19.80	80.1			
At 30°C.					
0.00	38.48		0.00	22.89	
33.65	30.51		20.76	22.89	
48.32	29.63		31.36	23.35	
66.11	28.78		50.99	23.61	
84.90	28.04		74.00	24.35	
100.00	27.57		100.00	25.57	
Ethyl Alcohol-1,4-Dioxane			Methanol-1,4-Dioxane		
Mole % ethyl alcohol	δ , dynes/cm.	$t^\circ\text{C}$.	Mole % methanol	δ , dynes/cm.	$t^\circ\text{C}$.
At Boiling Point					
0.00	21.59	101.5	0.00	21.59	101.5
14.54	22.52	90.6	14.00	23.89	74.2
27.64	22.05	85.2	29.85	24.72	69.5
45.15	20.15	81.7	43.95	23.18	68.1
64.07	18.97	79.6	51.40	22.33	67.8
74.01	18.33	78.9	62.31	21.34	67.2
87.95	17.27	78.2	84.37	19.64	65.6
100.00	16.47	78.35	92.38	18.82	65.1
			100.00	17.41	64.75
At 30°C.					
0.00	32.20		0.00	32.20	
21.01	30.20		22.50	31.65	
58.22	26.02		41.15	28.93	
70.56	24.15		66.20	25.98	
96.53	21.52		92.30	22.67	
100.00	21.48		100.00	21.69	

Equipment. It was necessary to develop a unique apparatus and procedure for this part of the investigation. The equipment and procedure are described completely elsewhere (11).

Results. Interfacial tension as a function of composition at the normal boiling point and at 30°C. for six of the binaries are reported in Table IV and plotted in Figures 1 through 3. Data on the other two systems have been reported (11).

The precision of measurement for the various systems is

estimated as follows: 0.5 dyne per cm. for the systems benzene-2-chloroethanol, ethyl alcohol-1,4-dioxane, and methanol-1,4-dioxane; 0.2 dyne per cm. for water-1-butanol, acetone-1-butanol, and carbon tetrachloride-1-propanol.

LIQUID VISCOSITIES

Kinematic viscosities of the eight binary mixtures were determined at several temperatures near the bubble points of the liquid mixtures at various compositions. Absolute viscosities were calculated and are reported.

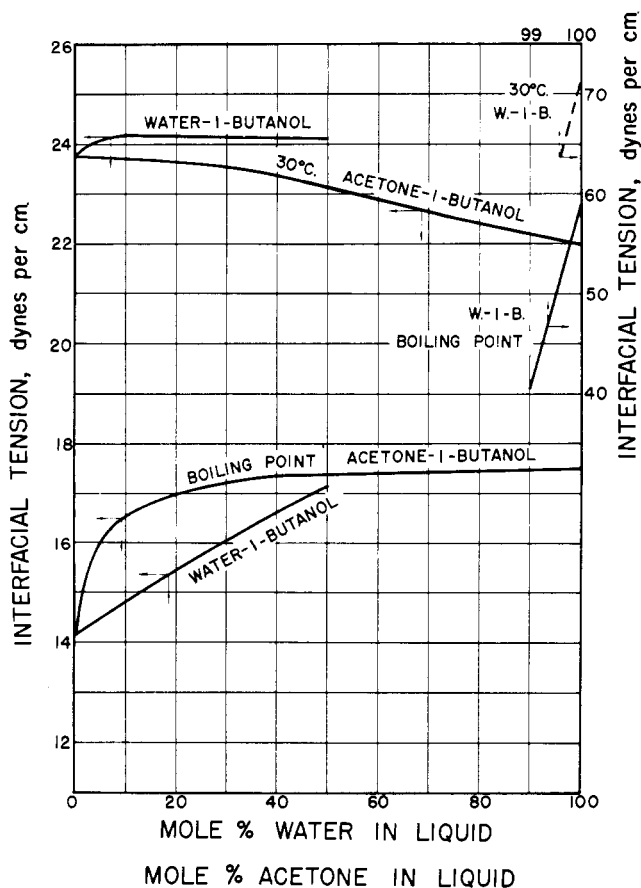


Figure 1. Interfacial tension of water-1-butanol system and acetone-1-butanol system

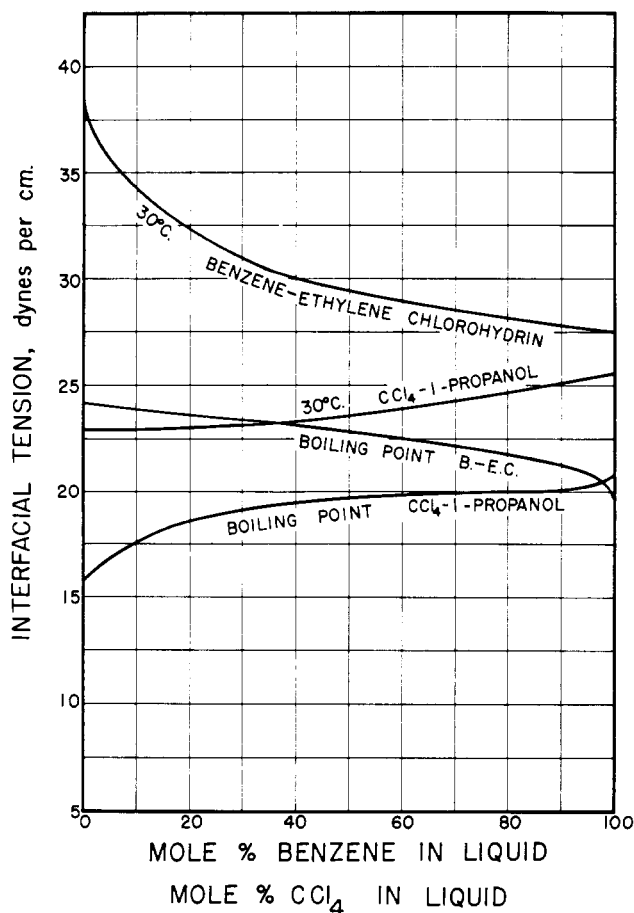


Figure 2. Interfacial tension of benzene-ethylene chlorohydrin system and carbon tetrachloride-propanol system

The Cannon and Fenske (5) modified Ostwald viscometer method (2) was used to determine the liquid mixture kinematic viscosities. Kinematic viscosity is defined as the quotient of the absolute viscosity divided by the density of the material at the same temperature and is expressed as centistokes or stokes.

For the Cannon-Fenske viscometer, the following equation applies.

$$\text{Kinematic viscosity, centistokes} = Ct - B/t \quad (1)$$

where

C = viscometer constant
 t = observed efflux time, seconds
 B = viscometer coefficient

For viscometers for which the B/t term is 0.1% of the Ct term or less, the B/t term may be neglected.

Three ASTM No. 25 Cannon-Fenske modified Ostwald viscometers were used to determine the liquid viscosities in this investigation. Water was utilized as the calibration fluid for the viscometers.

The liquid viscosities for the eight binary systems were measured at 30°, 55°, 75°, and 95°C. The viscosity measurement for several samples was limited to only 30°, 55°, and 75°C. because of evaporation of the sample in the temperature bath.

The kinematic viscosity of water was calculated from the absolute viscosity and liquid density data in the literature. The viscometer constant was calculated as

$$C = \frac{V_k, \text{ centistokes}}{t, \text{ seconds}} \quad (2)$$

Kinematic Viscosity of Water			
Temp., °C.	η , Centipoise (10)	ρ , Gram/Cc. (10)	V_k , Centistoke
30.0	0.8004	0.99567	0.80388
55.0	0.5073	0.98573	0.51464
75.0	0.3806	0.97489	0.39040
95.0	0.2994	0.96192	0.31125

Average Viscometer Constant, C	
Viscometer	C
G-3	0.003142
G-19	0.003955
G-20	0.003550

Discussion of Liquid Viscosity Data. Values of absolute viscosity are presented as a function of liquid composition and temperatures of 30°, 55°, 75°, and 95°C. in Table V. A precision of 0.2% was estimated in the measurement of liquid viscosity.

The graphically extrapolated values for liquid viscosity at the boiling points are also presented in Table VI. In the systems acetone-1-butanol; benzene-2-chloroethanol; ethyl alcohol-1,4-dioxane; and methanol-1,4-dioxane, the addition of the more volatile component to the less volatile component of the system at a constant temperature decreases the viscosity of the liquid mixture. For all systems, the higher the temperature, the lower is the liquid viscosity for the same liquid composition. Two major effects on liquid mixture viscosity at the boiling point are observed when the more volatile component is added to the less volatile component or mixtures of lower volatility.

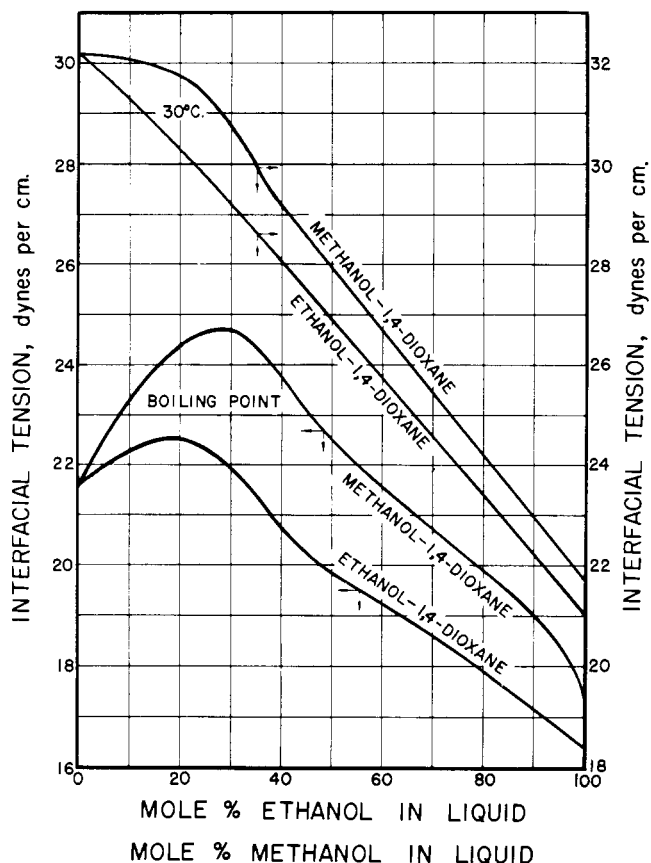


Figure 3. Interfacial tension of ethyl alcohol-1,4-dioxane system and methanol-1,4-dioxane system

The addition of the more volatile component lowers the boiling temperature and because of the decrease in temperature, increases the viscosity. Also, in most cases, the addition of the more volatile component lowers the viscosity of the mixture because the lighter component is less viscous (exceptions: 1-propanol-water, toluene-*n*-octane).

Apparently, at low concentration of the more volatile component in the liquid mixture, the lowered boiling point effect overshadows the decrease in viscosity effect. Therefore, at the lower concentrations of the more volatile component, the boiling point viscosity increases as the concentration of the more volatile component is increased from zero. When the influence of the composition at a higher concentration of the more volatile component due to viscosity effect becomes more important than the boiling point lowering effect, the liquid viscosity at the boiling point starts to decrease. Thus, a maximum of the liquid viscosity at the boiling point may be noted from the data.

Normal Boiling Points of Binary Systems. The normal boiling point-composition data for most of the systems investigated are reported in the literature.

System	Reference
1-Propanol-water	(7)
Toluene- <i>n</i> -octane	(3)
Water-1-butanol	(17)
Benzene-ethylene chlorhydrin	(16)
Carbon tetrachloride-1-propanol	(6)
Ethyl alcohol-1,4-dioxane	(8)
Methanol-1,4-dioxane	(13)

Table V. Liquid Viscosity as a Function of Temperature and Composition				
Liquid Compn., Mole %	Viscosity, Centipoises			
	30 °C.	55 °C.	75 °C.	95 °C.
1-Propanol				
1-Propanol-Water				
0.0	0.8004(20)	0.5073(20)	0.3806(20)	0.2994(20)
2.45	1.069	0.617	0.445	0.333
7.60			0.572	0.313
10.19	1.793	0.926	0.625	
22.31	2.346	1.127	0.740	
57.73	2.054	1.090	0.725	
79.70	1.861	1.032	0.693	
100.0	1.728	1.011	0.682	
Toluene				
Toluene-<i>n</i>-Octane				
0.0	0.4865(13)	0.3740(13)	0.3134(13)	0.2658(13)
26.34	0.470	0.375	0.302	0.255
41.84	0.464	0.362	0.297	0.252
82.82	0.485	0.373	0.309	0.266
88.80	0.498	0.378	0.316	0.270
94.17	0.508	0.384	0.322	0.274
100.00	0.520	0.398	0.330	0.280
Water				
Water-1-Butanol				
0.00	2.250	1.265	0.841	0.579
9.50	2.236	1.237	0.825	0.576
25.26	2.272	1.245	0.822	0.574
43.85	2.420	1.289	0.845	0.584
(Two liquid phase region)				
98.704	0.968	0.575	0.421	0.325
100.0	0.8004(20)	0.5073(20)	0.3806(20)	0.2994(20)
Acetone				
Acetone-1-Butanol				
0.00	2.250	1.265	0.841	0.579
11.52	1.535	0.932	0.655	0.482
23.07	1.127	0.722	0.529	
33.41	0.879	0.589	0.450	
46.85	0.642	0.455		
70.32	0.427	0.286		
79.74	0.368	0.320		
100.00	0.295	0.229		
Benzene				
Benzene-2-Chloroethanol				
0.0	2.624	1.472	1.018	0.748
33.65	1.315	0.822	0.615	
48.32	1.008	0.657	0.510	
66.11	0.771	0.530	0.416	
84.90	0.613	0.436	0.355	
100.00	0.562	0.410	0.333	
CCl₄				
Carbon Tetrachloride-1-Propanol				
0.0	1.728	1.011	0.681	
20.76	2.078	1.207	0.839	
31.36	1.650	0.970	0.683	
50.99	1.113	0.713	0.521	
74.00	0.947	0.553		
100.0	0.841	0.618	0.510	
Ethyl Alcohol				
1,4-Dioxane				
0.0	1.096	0.758	0.597	0.489
21.01	0.984	0.677	0.522	
58.22	0.825	0.566	0.414	
70.56	0.798	0.546	0.396	
96.53	0.927	0.612	0.450	
100.0	0.988	0.643	0.470	
Methanol				
1,4-Dioxane				
0.00	1.096	0.758	0.597	0.489
22.50	0.877	0.616	0.487	
41.15	0.733	0.521		
66.20	0.603	0.432		
92.30	0.520	0.382		
100.0	0.509	0.370		

Table VI. Liquid Viscosity at Boiling Point

Liquid Compn., Mole %	Boiling Point, C.	Viscosity, Centipoise
1-Propanol		
1-Propanol-Water		
0.00	100.00	0.284
1.00	95.00	0.313
2.00	92.00	0.340
4.00	90.40	0.375
6.00	89.30	0.434
10.00	88.50	0.510
20.00	88.10	0.590
30.00	87.90	0.593
40.00	87.79	0.594
43.20	87.78	0.588
50.00	87.90	0.587
60.00	88.30	0.572
70.00	89.14	0.560
80.00	90.50	0.539
85.00	91.50	0.524
90.00	92.80	0.507
96.00	95.00	0.483
100.00	97.19	0.445
Toluene		
Toluene-n-Octane		
0.00	125.665	0.210
2.50	123.43	0.212
5.00	122.50	0.212
10.00	121.20	0.212
15.00	119.92	0.2122
20.00	118.75	0.2124
25.00	117.68	0.2125
30.00	116.72	0.2125
40.00	115.16	0.2125
50.00	113.94	0.2145
60.00	112.97	0.2195
70.00	112.10	0.2270
80.00	111.30	0.2350
90.00	110.57	0.2410
95.00	110.25	0.2450
100.00	110.623	0.2475
Water		
Water-1-Butanol		
0.0	117.8	0.388
5.0	110.15	0.450
10.0	105.92	0.480
15.0	102.68	0.506
50.0	100.15	0.527
30.0	96.45	0.562
40.0	94.64	0.584
50.0	93.45	0.614
98.0	93.00	0.349
99.0	94.05	0.320
99.5	96.60	0.303
100.0	100.0	0.284
Acetone		
Acetone-1-Butanol		
0.00	117.8	0.388
1.00	115.7	0.395
2.50	113.1	0.409
5.00	109.1	0.425
10.00	102.0	0.445
15.00	96.0	0.452
20.00	90.8	0.457
25.00	86.2	0.444
30.00	82.39	0.434
35.00	79.00	0.420
40.00	76.28	0.405
50.00	71.8	0.364
60.00	67.96	0.329
70.00	64.60	0.304
80.00	61.62	0.279
90.00	58.79	0.253
95.00	57.50	0.240
100.00	56.11	0.228
Benzene		
Benzene-2-Chloroethanol		
0.00	128.6	0.475
1.00	115.90	0.560
2.50	108.31	0.605
5.00	99.92	0.665
10.00	93.00	0.685
15.00	89.70	0.668

Table VI. (Cont.)

Liquid Compn., Mole %	Boiling Point, C.	Viscosity, Centipoise
Benzene		
Benzene-2-Chloroethanol		
<i>(Cont.)</i>		
20.00	89.68	0.639
30.00	85.45	0.574
40.00	84.12	0.508
50.00	83.11	0.460
60.00	82.35	0.413
70.00	81.74	0.379
80.00	81.20	0.347
85.00	80.82	0.337
90.00	80.54	0.332
95.00	80.27	0.323
100.00	80.08	0.317
CCl₄		
CCl₄-1-Propanol		
0.0	97.19	0.445
5.0	91.65	0.580
10.0	87.46	0.697
15.0	84.07	0.793
20.0	81.70	0.766
30.0	78.30	0.666
40.0	76.34	0.592
50.0	75.07	0.528
60.0	74.27	0.471
70.0	73.69	0.453
80.0	73.40	0.454
85.0	73.54	0.459
90.0	73.83	0.473
95.0	74.20	0.490
97.50	74.86	0.499
100.0	76.75	0.487
Ethyl Alcohol		
Ethyl Alcohol-1,4-Dioxane		
0.0	101.50	0.460
5.0	96.87	0.465
10.0	93.44	0.461
15.0	90.64	0.456
20.0	88.00	0.452
30.0	84.24	0.438
40.0	82.42	0.417
50.0	81.11	0.397
60.0	80.11	0.377
70.0	79.28	0.365
80.0	78.62	0.368
85.0	78.36	0.383
90.0	78.18	0.399
95.0	78.11	0.426
97.5	78.18	0.436
100.0	78.35	0.441
Methanol		
Methanol-1,4-Dioxane		
0.00	101.50	0.460
5.00	92.90	0.482
10.00	86.10	0.495
15.00	81.65	0.491
20.00	79.10	0.481
30.00	75.30	0.463
40.00	72.61	0.441
50.00	70.58	0.416
60.00	68.88	0.395
70.00	76.42	0.376
80.00	66.21	0.358
90.00	65.33	0.343
100.00	64.75	0.329

Because of some possible inconsistencies in some of the data the normal boiling point-composition data for two binary systems were determined by the authors by means of the Cottrell-Washburn-Read boiling point apparatus (19). Results for the acetone-1-butanol system are presented in Table VII and those for the methanol-1,4-dioxane system in Table VIII.

The authors' normal boiling point-composition values for the methanol-1,4-dioxane system are somewhat different from those of Padgitt, Amis, and Hughes (13). The values determined by the authors were used in the calculations for this project.

Table VII. Boiling Point for System Acetone-1-Butanol

Boiling Point, C.	Liquid Compn., Mole % Acetone
117.8	0.0
98.73	12.22
88.03	23.65
80.01	33.25
71.52	50.30
67.32	61.72
61.96	78.55
59.07	89.11
56.11	100.00

Table VIII. Normal Boiling Point for Methanol-1,4-Dioxane System

Liquid Compn., Mole % Methanol	Boiling Point, C.
0.00	101.50
7.57	90.50
13.95	83.24
25.53	76.96
33.50	74.50
35.75	73.60
43.69	71.80
46.35	71.50
50.21	70.38
63.97	68.20
75.38	66.74
81.59	66.18
87.89	65.50
100.0	64.75

VAPOR VISCOSITY

Vapor viscosities of the binary mixtures at temperatures above the dew points were determined for various compositions. It was necessary to develop a special type of apparatus for this purpose. This viscometer and the procedure followed in determining the viscosities have been described (11).

Vapor viscosity-composition-temperature data are reported here on the following systems (Table IX): water-1-butanol; acetone-1-butanol; benzene-ethylene chlorohydrin; carbon tetrachloride-1-propanol; ethyl alcohol-1,4-dioxane; and methanol-1,4-dioxane. Similar data are reported on the 1-propanol-water and toluene-*n*-octane systems (11).

Discussion of Vapor Viscosity. The vapor viscometer was designed to utilize Poiseuille's equation (15) and the apparatus was calibrated using air as a reference material. Average values of air viscosity reported by Myerson and Eicher (12) and Ling (11) were utilized. The viscosities were then calculated from the experimental data by means of the following equation (11):

$$\frac{\eta_g}{\eta_a} = \frac{[(p_{1i} - p_{1f})^2 - (p_{2i} - p_{2f})^2]_g t_g (\Delta p_2)_a}{[(p_{1i} - p_{1f})^2 - (p_{2i} - p_{2f})^2]_a t_a (\Delta p_2)_g} \quad (3)$$

From a consideration of possible experimental errors and the precision of the measurements, it is believed the viscosities were determined with a possible maximum deviation of 4%.

ACKNOWLEDGMENT

The authors wish to express their appreciation to the National Science Foundation for its aid in carrying out this and related investigations.

LITERATURE CITED

- (1) Amis, E. S., Choppin, A. R., Padgitt, F. L., *J. Am. Chem. Soc.* **64**, 1207 (1942).
- (2) Am. Soc. Testing Materials, Philadelphia, Pa., Committee D-2, "ASTM Standards on Petroleum Products and Lubricants," 1953.
- (3) Berg, L., Popovac, D. O., *Chem. Eng. Progr.* **45**, 683 (1949).
- (4) Brunjes, A. S., Fumas, C. C., *Ind. Eng. Chem.* **27**, 396 (1935).
- (5) Cannon, M. R., Fenske, M. R., *Ind. Eng. Chem., Anal. Ed.* **10**, 297 (1938).

Table IX. Vapor Viscosity as a Function of Temperature and Composition

Vapor Compn., y_1 , Mole %	Vapor Viscosity, Poises $\times 10^5$		
	110°C.	130°C.	150°C.
Water			
0.00	8.91	9.22	9.47
9.50	9.03	9.34	9.57
25.26	9.25	9.58	9.87
43.85	9.60	9.99	10.33
98.704	12.55	13.24	13.86
100.00	12.81	13.53	14.25
Acetone			
0.00	8.91	9.22	9.47
11.52	9.02	9.35	9.62
23.07	9.14	9.47	9.75
33.41	9.25	9.57	9.89
46.85	9.38	9.73	10.06
70.32	9.66	10.05	10.42
79.74	9.79	10.18	10.57
100.0	10.11	10.54	10.98
Benzene			
0.00	12.38	12.84	13.31
33.65	11.63	12.06	12.49
48.32	11.34	11.74	12.16
66.11	11.01	11.40	11.78
84.90	10.68	11.04	11.42
100.00	10.45	10.79	11.15
CCl ₄			
0.00	10.42	10.83	11.24
20.76	11.44	11.84	12.21
31.36	11.88	12.27	12.65
50.99	12.55	12.95	13.37
74.00	13.09	13.55	14.01
100.0	13.58	14.10	14.63
Ethyl Alcohol			
0.00	17.01	17.56	18.1.
21.01	16.21	16.80	17.20
58.22	14.54	14.97	15.42
70.56	13.86	14.28	14.71
96.53	12.22	12.64	13.08
100.0	11.96	12.39	12.83
Methanol			
0	17.01	17.56	18.11
22.50	16.50	16.98	17.48
41.15	15.98	16.42	16.90
66.20	14.99	15.45	15.88
92.30	13.37	13.86	14.35
100.0	12.82	13.32	13.83

- (6) Carley, J. F., Bertlesen, III, L. W., *Ind. Eng. Chem.* **41**, 2806 (1949).
- (7) Gadwa, T. W., "Rectification of Binary Mixtures," chemical engineering thesis, Massachusetts Institute of Technology, 1936.
- (8) Hopkins, R. N., Yerger, E. S., Lynch, C. C., *J. Am. Chem. Soc.* **61**, 2460 (1939).
- (9) Kirk, R. E., Othmer, D. F., "Encyclopedia of Chemical Technology," Interscience Encyclopedia, New York, 1947-55.
- (10) Lange, N. A., Forker, G. M., Burington, R. S., "Handbook of Chemistry," 6th ed., Handbook Publishers, Sandusky, Ohio, 1952.
- (11) Ling, T. D., Van Winkle, M., *Ind. Eng. Chem., Chem. Eng. Data Series* **3**, 82 (1958).
- (12) Myerson, A. L., Eicher, J. H., *J. Am. Chem. Soc.* **74**, 2758 (1952).
- (13) Padgitt, F. L., Amis, E. S., Hughes, D. W., *Ibid.*, **64**, 1231 (1942).
- (14) Pesee, B., Evdokimoff, B., *Gazz. chim. ital.* **70**, 716 (1940).
- (15) Poiseuille, J. L. M., *Compt. rend.* **11**, 961, 104 (1840).
- (16) Snyder, H. B., Gilbert, E. C., *Ind. Eng. Chem.* **34**, 1519 (1942).
- (17) Stockhardt, J. S., Hull, C. M., *Ibid.*, **23**, 1438 (1931).
- (18) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, New York, 1950.
- (19) Washburn, E. W., Read, J. W., *J. Am. Chem. Soc.* **41**, 729 (1919).
- (20) Wilke, C. R., *J. Chem. Phys.* **18**, 517 (1950).

Received for review August 23, 1956. Accepted April 8, 1957.