Table II. Comparison of Surface Tensions of Zapior (*10*) and Equation 1 for $T = 22°$ C.

Wt. % M.E.K.	Surface Tension, Dyne/Cm. Zapior	Equation 1
0.037	71.77	72.12
0.070	71.05	71.68
0.36	67.91	68.91
0.43	67.21	68.05
0.58	65.98	66.74
0.70	64.98	65.78
1.45	62.58	60.38

The values of b calculated from the experimental data are tabulated in Table I for the six average concentrations. Equation 1 reproduces the data for all concentrations with a standard deviation of 0.28 dyne per cm.

A comparison of surface tensions measured by Zapior (*10*), who measured the relative surface tensions of solutions of M.E.K. in a $0.1N$ KCl solvent at 22° C., with surface tensions calculated from Equation 1 is presented in Table II. The effect of the presence of $0.1N$ KCl on the surface tension of the M.E.K.-water mixtures is not known. In the absence of M.E.K., the surface tension of a $0.1N$ KCl solution is greater than that of pure water by 0.155 dyne per cm. at 20° C. (*4*).

No attempt was made to calculate theoretically the surface tensions of the nonathermal water-methyl ethyl ketone mixtures.

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Refraction, Dispersion, and Densities of Benzene, Toluene, and Xylene Mixtures

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Continuing a study of the effect of molecular structure on refractive index–density relationships, mixtures of the three possible combinations of the aromatics benzene, toluene, and xylene were investigated in the present work.

THE EFFECTS of composition and temperature on refractive index, dispersion, and density measurements are presented for the mixtures of benzene-toluene, benzene-xylene, and toluene-xylene. Refractive index measurements for sodium D and hydrogen F and C lines were determined with the density measurements at 20°, 30°, and 40° C. Density measurements provide a satisfactory means of analysis for the benzene-toluene and benzene-xylene systems but not for the toluene-xylene system. The benzene-toluene system may also be analyzed using refractive index measurements. Deviations from linearity limit the use of refractive index measurements for the other systems. Among the physical properties presented, dispersion ($n_F - n_C$) measurements are recommended for use in the analysis of all the binary systems presented. Refractivity intercept plots ($n_D - d/2$) *vs.* composition are recommended to produce a linear relationship between the variables. Linearity of these plots may be attributed to the similarity, in structure, of the compounds used. Statistical methods were employed in determining the slopes and the intercepts of the straight lines used to present the refractivity intercept data.

PREPARATION

The chemicals used were Baker and Adamson ACS reagent grade and all contained less than 0.02% water and residues after evaporation of less than 0.002%. Boiling points at 760 mm. of Hg were as follows: benzene (Code 1442) 80.1° C.; toluene (Code 2398) 110.6° C.; and xylene (Code 2415) 138.5° C. Within the limits of the experimental procedure, the refractive indices and the densities of the compounds were in good agreement with those reported (*8*). The xylene used was a mixture of isomers; therefore, there were no values available for comparison.

Solutions covering the entire composition range at approximately 10 wt. % increments were prepared according to the established procedure (*10*) of weighing the liquids. Based on the amounts of material and the weighing precision possible, compositions were known to within ±0.001%.

Table I. Benzene-Toluene System

Benzene Composition		Density,	Refractive Index Measurements ±0.00003			Dispersion,	Refractivity Intercept,
Wt. %	Vol. %	d, G./Ml.	n_D	n_F	n_C	$n_F - n_C$	$n_D - d/2$
20° C.							
0.00	0.00	0.8666	1.49780	1.51115	1.49138	0.01977	1.0645
9.90	9.78	0.8670	1.49800	1.51147	1.49174	0.01973	1.0645
19.98	19.76	0.8678	1.49824	1.51171	1.49204	0.01967	1.0644
29.90	29.62	0.8690	1.49858	1.51196	1.49233	0.01963	1.0641
39.99	39.67	0.8701	1.49897	1.51220	1.49267	0.01953	1.0639
50.00	49.66	0.8716	1.49926	1.51263	1.49312	0.01951	1.0634
60.02	59.70	0.8730	1.49969	1.51311	1.49370	0.01941	1.0632
69.84	69.55	0.8739	1.50014	1.51355	1.49418	0.01937	1.0632
80.01	79.79	0.8757	1.50062	1.51403	1.49477	0.01926	1.0628
90.66	90.54	0.8771	1.50114	1.51456	1.49535	0.01921	1.0626
100.00	100.00	0.8784	1.50185	1.51518	1.49607	0.01911	1.0626
30° C.							
0.00	0.00	0.8573	1.49220	1.50559	1.48558	0.02001	1.0635
9.90	9.79	0.8583	1.49230	1.50574	1.48573	0.02001	1.0632
19.98	19.78	0.8592	1.49250	1.50594	1.48603	0.01991	1.0629
29.90	29.64	0.8602	1.49270	1.50618	1.48633	0.01985	1.0626
39.99	39.70	0.8611	1.49304	1.50648	1.48663	0.01985	1.0625
50.00	49.69	0.8622	1.49339	1.50672	1.48697	0.01975	1.0623
60.02	59.73	0.8632	1.49374	1.50702	1.48737	0.01965	1.0622
69.84	69.58	0.8641	1.49408	1.50741	1.48776	0.01965	1.0620
80.01	79.81	0.8657	1.49452	1.50780	1.48821	0.01959	1.0617
90.66	90.50	0.8666	1.49496	1.50824	1.48880	0.01944	1.0616
100.00	100.00	0.8680	1.49540	1.50863	1.48929	0.01934	1.0614
40° C.							
0.00	0.00	0.8480	1.48676	1.50022	1.48000	0.02022	1.0627
9.90	9.80	0.8491	1.48671	1.50027	1.48000	0.02027	1.0622
19.98	19.80	0.8498	1.48688	1.50032	1.48020	0.02027	1.0620
29.90	29.65	0.8504	1.48704	1.50057	1.48047	0.02010	1.0618
39.99	39.72	0.8514	1.48737	1.50071	1.48069	0.02002	1.0617
50.00	49.71	0.8522	1.48757	1.50098	1.48096	0.02002	1.0615
60.02	59.75	0.8530	1.48792	1.50127	1.48133	0.01994	1.0614
69.84	69.61	0.8540	1.48817	1.50152	1.48163	0.01989	1.0612
80.01	79.83	0.8548	1.48847	1.50188	1.48198	0.01990	1.0611
90.66	90.47	0.8559	1.48887	1.50221	1.48242	0.01975	1.0609
100.00	100.00	0.8572	1.48937	1.50267	1.48304	0.01963	1.0607

Table II. Benzene-Xylene System

Benzene Composition		Density,	Refractive Index Measurements ±0.00003			Dispersion,	Refractivity Intercept,
Wt. %	Vol. %	d, G./Ml.	n_D	n_F	n_C	$n_F - n_C$	$n_D - (d/2)$
20° C.							
0.00	0.00	0.8663	1.49868	1.51225	1.49250	0.02020	1.0655
10.00	9.88	0.8668	1.49858	1.51214	1.49203	0.02011	1.0652
19.14	18.93	0.8674	1.49866	1.51215	1.49209	0.02004	1.0650
31.07	30.78	0.8680	1.49872	1.51220	1.49223	0.01997	1.0647
40.19	39.86	0.8688	1.49887	1.51229	1.49243	0.01986	1.0645
50.43	50.08	0.8704	1.49921	1.51258	1.49282	0.01976	1.0640
59.74	59.40	0.8715	1.49951	1.51282	1.49316	0.01966	1.0638
70.26	69.97	0.8730	1.49984	1.51321	1.49369	0.01952	1.0633
79.92	79.70	0.8746	1.50033	1.51370	1.49423	0.01947	1.0630
89.72	89.59	0.8764	1.50095	1.51432	1.49501	0.01931	1.0627
100.00	100.00	0.8784	1.50185	1.51518	1.49607	0.01911	1.0626
30° C.							
0.00	0.00	0.8579	1.49359	1.50721	1.48677	0.02044	1.0647
10.00	9.89	0.8581	1.49339	1.50697	1.48663	0.02034	1.0643
19.14	18.96	0.8584	1.49334	1.50687	1.48663	0.02024	1.0641
31.07	30.82	0.8592	1.49329	1.50682	1.48663	0.02019	1.0637
40.19	39.91	0.8600	1.49339	1.50687	1.48682	0.02005	1.0634
50.43	50.13	0.8610	1.49349	1.50702	1.48702	0.02000	1.0630
59.74	59.45	0.8620	1.49374	1.50716	1.48732	0.01984	1.0627
70.26	70.01	0.8632	1.49398	1.50746	1.48772	0.01974	1.0624
79.92	79.73	0.8645	1.49437	1.50775	1.48811	0.01964	1.0621
89.72	89.61	0.8661	1.49468	1.50829	1.48880	0.01949	1.0619
100.00	100.00	0.8680	1.49540	1.50863	1.48929	0.01934	1.0614

(Continued on page 32)

Table II. Benzene-Xylene System (*Continued*)

Benzene Composition		Density, d, G./Ml.	Refractive Index Measurements ±0.00003			Dispersion, $n_F - n_C$	Refractivity Intercept, $n_D - (d/2)$
Wt. %	Vol. %		n_D	n_F	n_C		
40° C.							
0.00	0.00	0.8494	1.48862	1.50207	1.48072	0.02135	1.0639
10.00	9.92	0.8494	1.48817	1.50182	1.48052	0.02130	1.0635
19.14	19.00	0.8496	1.48807	1.50167	1.48042	0.02125	1.0633
31.07	30.87	0.8503	1.48787	1.50147	1.48037	0.02110	1.0627
40.19	39.97	0.8509	1.48787	1.50137	1.48042	0.02095	1.0624
50.43	50.20	0.8516	1.48792	1.50142	1.48052	0.02090	1.0621
59.74	59.51	0.8525	1.48807	1.50142	1.48056	0.02086	1.0618
70.26	70.06	0.8534	1.48822	1.50162	1.48087	0.02075	1.0615
79.92	79.77	0.8547	1.48837	1.50177	1.48118	0.02059	1.0610
89.72	89.63	0.8560	1.48877	1.50207	1.48153	0.02054	1.0608
100.00	100.00	0.8572	1.48937	1.50267	1.48304	0.01963	1.0607

Table III. Toluene-Xylene System

Toluene Composition		Density, d, G./Ml.	Refractive Index Measurements ±0.00003			Dispersion, $n_F - n_C$	Refractivity Intercept, $n_D - (d/2)$
Wt. %	Vol. %		n_D	n_F	n_C		
20° C.							
0.00	0.00	0.8663	1.49868	1.51225	1.49205	0.02020	1.0655
9.74	9.74	0.8664	1.49858	1.51215	1.49199	0.02016	1.0654
20.01	20.01	0.8663	1.49834	1.51196	1.59184	0.02012	1.0652
30.02	30.01	0.8663	1.49824	1.51181	1.49170	0.02011	1.0651
40.12	40.12	0.8663	1.49820	1.51168	1.49162	0.02006	1.0650
49.95	49.94	0.8663	1.49799	1.51160	1.49156	0.02004	1.0650
59.97	59.96	0.8663	1.49785	1.51147	1.49150	0.01997	1.0647
70.14	70.13	0.8664	1.49775	1.51132	1.49141	0.01991	1.0646
79.78	79.77	0.8664	1.49766	1.51127	1.49137	0.01990	1.0645
89.92	89.92	0.8664	1.49761	1.51117	1.49131	0.01986	1.0644
100.00	100.00	0.8666	1.49780	1.51115	1.49138	0.01977	1.0645
30° C.							
0.00	0.00	0.8579	1.49359	1.50721	1.48677	0.02044	1.0647
9.74	9.74	0.8578	1.49339	1.50702	1.48663	0.02039	1.0644
20.01	20.02	0.8578	1.49319	1.50682	1.48644	0.02038	1.0643
30.02	30.03	0.8578	1.49304	1.50667	1.48633	0.02034	1.0641
40.12	40.14	0.8577	1.49289	1.50648	1.48615	0.02033	1.0640
49.95	49.96	0.8576	1.49275	1.50633	1.48608	0.02025	1.0640
59.97	59.98	0.8575	1.49255	1.50618	1.48598	0.02020	1.0638
70.14	70.15	0.8574	1.49246	1.50609	1.48588	0.02021	1.0638
79.78	79.79	0.8574	1.49230	1.50589	1.48578	0.02011	1.0636
89.92	89.93	0.8573	1.49225	1.50578	1.48573	0.02006	1.0636
100.00	100.00	0.8573	1.49220	1.50559	1.48558	0.02001	1.0625
40° C.							
0.00	0.00	0.8494	1.48862	1.50207	1.48072	0.02135	1.0639
9.74	9.75	0.8493	1.48832	1.50202	1.48118	0.02079	1.0637
20.01	20.04	0.8492	1.48812	1.50177	1.48110	0.02067	1.0636
30.02	30.05	0.8491	1.48792	1.50152	1.48092	0.02060	1.0634
40.12	40.16	0.8491	1.48767	1.50127	1.48077	0.02050	1.0631
49.95	49.99	0.8486	1.48757	1.50117	1.48072	0.02045	1.0632
59.97	60.01	0.8484	1.48734	1.50092	1.48057	0.02035	1.0632
70.14	70.17	0.8483	1.48711	1.50067	1.48033	0.02034	1.0629
79.78	79.80	0.8482	1.48701	1.50052	1.48022	0.02030	1.0629
89.92	89.94	0.8481	1.48691	1.50047	1.48011	0.02036	1.0628
100.00	100.00	0.8480	1.48676	1.50022	1.48000	0.02022	1.0627

MEASUREMENTS

Densities and the refractive indices of the prepared solutions were determined in duplicate at 20°, 30°, and 40° C. The temperature was controlled to within ±0.02° C. by a Fisher Isotemp constant temperature bath. A Bausch & Lomb precision refractometer was used with sodium and hydrogen (*1*) lamps to observe the refractive index. Calibration was checked using boiled demineralized water. Densities were determined by using calibrated 10-ml. Weld-type capped specific gravity bottles.

Data for the systems analyzed are presented with the calculated dispersions and refractivity intercepts in Tables I to III. Knowing the densities of the pure components and that of the mixtures, volume per cent was calculated from weight per cent assuming no volume change on mixing. The density-composition and refractive index–composition plots are shown in Figure 1.

Neither density nor refractive index plots provide a satisfactory analytical tool for the analysis of all the binary systems presented.

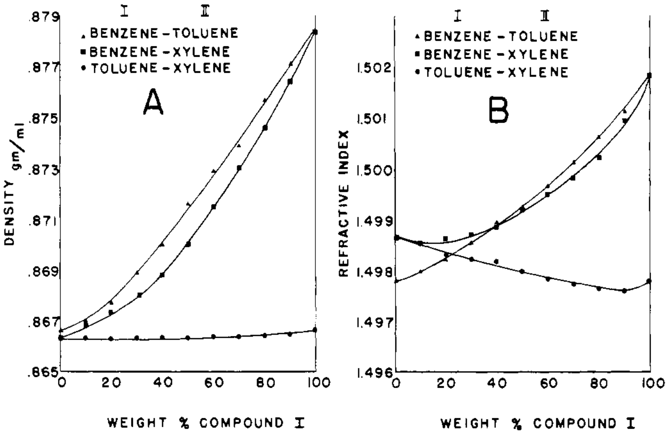

Figure 1. *A* Densities and *B* refractive indices of benzene-toluene, benzene-xylene, and toluene-xylene systems at 20° C.

Table IV. Constants for Pure Compounds

Equation	Temp., ° C.	Benzene	Toluene	Xylene
Eykman	20	0.7516	0.7560	0.7575
	30	0.7514	0.7547	0.7577
	40	0.7521	0.7565	0.7580
Gladstone-Dale	20	0.5714	0.5744	0.5756
	30	0.5708	0.5724	0.5758
	40	0.5709	0.5740	0.5753
Lorentz-Lorenz	20	0.3360	0.3381	0.3388
	30	0.3362	0.3379	0.3391
	40	0.3368	0.3390	0.3395
Newton	20	1.4296	1.4348	1.4383
	30	1.4242	1.4272	1.4348
	40	1.4211	1.4274	1.4318
Kurtz Refractivity intercept	20	1.0627	1.0645	1.0655
	30	1.0614	1.0625	1.0647
	40	1.0607	1.0627	1.0639

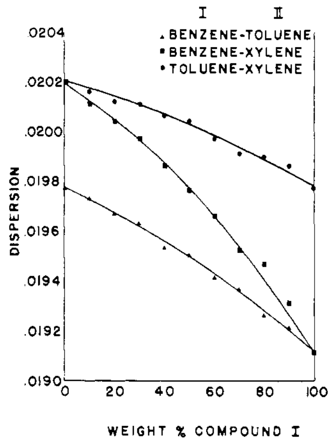

Figure 2. Dispersions of benzene-toluene, benzene-xylene, and toluene-xylene systems at 20° C.

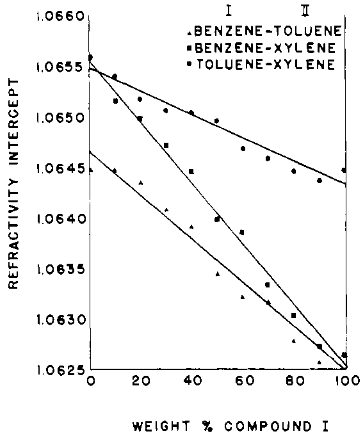

Figure 3. Refractivity intercepts of benzene-toluene, benzene-xylene, and toluene-xylene systems at 20° C.

DISCUSSION

An IBM 1410 computer was used to check the equations suggested by Newton (*9*), $n^2 - 1/d$; Gladstone-Dale (*4*), $n - 1/d$; Lorentz-Lorenz (*6, 7*) $(n^2 - 1/n^2 + 2) \times (1/d)$; Eykman (*3*) $(n^2 - 1/n^2 + 0.4) \times (1/d)$; and Kurtz (*5*) refractivity intercept, $n - d/2$, for independence of temperature. Of the five relationships tested, only that of Newton showed considerable variation with temperature. Refractivity intercept values decreased slightly with increase in temperature. Table IV shows the results of the relationships for the pure compounds. Constancy of the values indicates usefulness in temperature extrapolation or interpolation. Equations suggested by Gladstone-Dale, Lorentz-Lorenz, and Eykman can be satisfactorily used to calculate the refractive indices of the mixtures at various other temperatures. Equally satisfactory results obtained from these relationships may be attributed to the chemical structural similarity of the compounds used. For methanol solutions of aromatics, it was reported (*10*) that only the Eykman relationship produced satisfactory constancy in the same temperature range.

Dispersion data were suggested (*10*) as a useful property for use as a criterion of purity and as an indication of chemical structure. Dispersion measurements for this research were of the same order of magnitude owing to similarity of chemical structures. In the systems analyzed, $(n_F - n_C)$ dispersion increased with the temperature while the ratio of the two indices (n_F/n_C) remained relatively constant. A dispersion-composition plot is presented in Figure 2.

Refractivity intercept values were determined as suggested by Kurtz and Ward (*5*) at the temperatures used. The plot of refractivity intercept *vs.* composition produced a linear relationship similar to alcohol-water (*2*) and ethanolamine-water (*11*) systems. Statistical methods were employed in determining the slope and the intercept of the straight line used to present the data in Figure 3.

Density measurements are not useful in the analysis of mixtures in which compounds possess densities of the same order of magnitude. This is observed in Figure 1, *A*, where the similarity of the densities of toluene and xylene prevent the use of density measurements as an analytical tool. Refractive index measurements show linearity only for the benzene-toluene system.

Dispersion and refractivity intercept plots may be used satisfactorily in the analysis of the systems presented in this work.

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Vapor-Liquid Equilibrium Data for Benzene-Alkylbenzene Systems

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Isobaric vapor-liquid equilibrium data are reported for the following benzene-alkylbenzene systems: benzene-toluene, benzene-ethylbenzene, and benzene–*n*-propylbenzene. Within the experimental error, these systems obey Raoult's law.

THE SYSTEM benzene-toluene, the simplest member of the benzene-alkylbenzene class of mixtures, obeys Raoult's law closely (*6*). The purpose here is to present thermodynamic data for two other benzene-alkylbenzene systems: benzene-ethylbenzene and benzene–*n*-propylbenzene.

Equilibrium data at atmospheric pressure for the system benzene-ethylbenzene were obtained by Makh and Azarova (*3*), who reported an average relative volatility $\alpha = 7$. The theoretical value, assuming that Raoult's law is obeyed, is $\alpha = 5$. Makh and Azarova also studied the system benzene-toluene and reported a relative volatility $\alpha = 3.5$ (*3*). The theoretical value, assuming that Raoult's law is obeyed, is $\alpha = 2.4$. Since several other studies have shown that the system benzene-toluene obeys Raoult's law (*6*), the authors concluded that the data of Makh and Azarova contain serious errors.

EXPERIMENTAL

Chemicals. Reagents (Eastman Kodak Co.) were further purified by fractionation. The final properties of the reagents are recorded in Table I.

Apparatus. The equilibrium apparatus (Figure 1) is a recirculation type. The main components of the apparatus are the boiler, the vapor-liquid separator, the vapor condenser, the traps for the liquid and vapor condensate. The boiler is provided with internal and external heating units. Vapor generated within the boiler rises through the Cottrell tube and enters the separator. The separated liquid drops to the liquid trap, where samples are withdrawn using a hypodermic needle, and overflows back to the boiler.

Table I. Properties of Reagents

Material	Refractive Index at 25° C.		Boiling Point, ° C.	
	Experimental	Literature (*1*)	Experimental	Literature (*1*)
Benzene	1.49791	1.49792	80.08	80.100
Toluene	1.49413	1.49414	110.62	110.625
Ethylbenzene	1.49318	1.49320	136.18	136.186
n-Propylbenzene	1.48961	1.48951	159.24	159.217

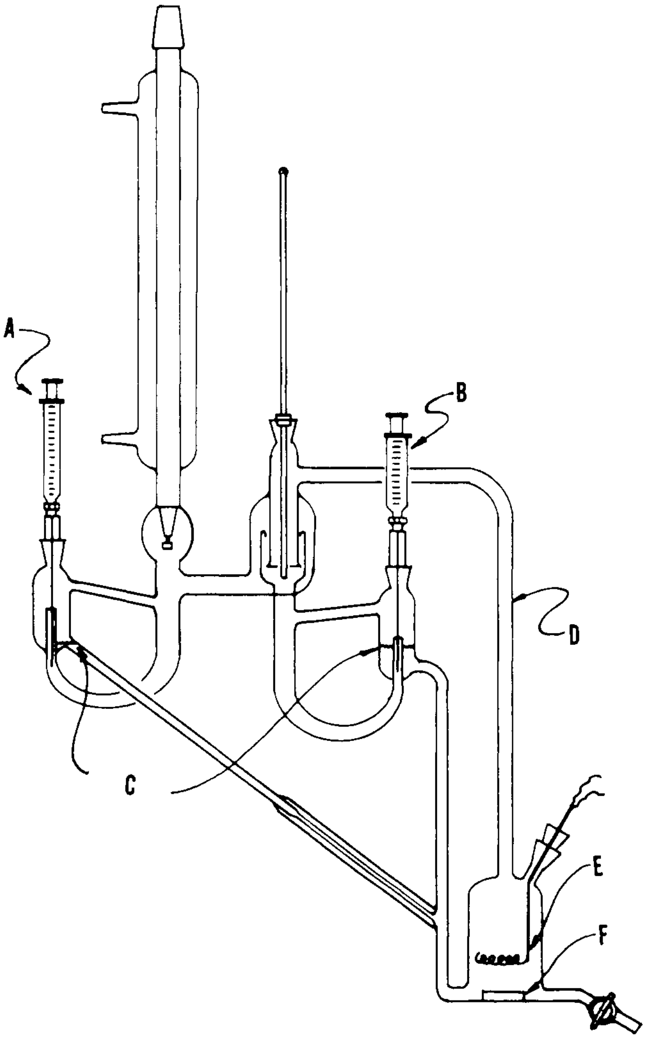

Figure 1. Diagram of equilibrium still

A. Condensate sample
B. Liquid sample
C. Operating levels
D. Cottrell tube
E. Internal heater
F. Stirrer