Table IV. Comparison of Results with Those Obtained by Bloom and Tricklebank (*1*)

Mole Fraction $CdCl_2$	$H_{823} - H_{300}$, Kcal./Mole		$H_{873} - H_{300}$, Kcal./Mole		$H_{923} - H_{300}$, Kcal./Mole	
	This work	Ref. (*1*)	This work	Ref. (*1*)	This work	Ref. (*1*)
0	16.08	15.60	17.41	16.65	18.74	17.80
0.3	16.39	15.75	17.76	17.05	19.12	18.30
0.5	16.75	16.10	18.10	17.40	19.44	18.70
0.7	17.09	16.70	18.45	17.80	19.80	18.90
1.0	17.74	17.25	19.04	18.25	20.34	19.30

Table V. Comparison of Heat Capacity Determinations

	Temp. Range, ° K.	C_p, Cal./Mole – ° K.			
		This work	Ref. (*1*)	Ref. (*6*)	Ref. (*11*)
$PbCl_2$ (solid)	300–773	20.4	19.8	20.2[a]	. . .
$PbCl_2$ (liquid)	774–963	26.6	22.6	27.2	. . .
$CdCl_2$ (solid)	300–840	19.7	18.9	20.2[b]	28.5[c]
$CdCl_2$ (liquid)	841–958	26.6	21.8	. . .	26.3[c]

[a] Average value from $C_p = 15.96 + 8 \times 10^{-3}T$. [b] Average value from $C_p = 14.54 + 9.6 \times 10^{-3}T$. [c] Temperature range 60° to 100° K. above and below the melting point.

indicate the properties calculated assuming ideal solutions.

Figure 1 shows that the enthalpy of mixing in this system is less than 200 cal. per mole. The entropy data indicate that the entropy of mixing is ideal assuming random mixing of the lead and cadmium ions.

Boardman, Darman, and Heymann (*2*) found negative deviations from additivity in molar volumes for the $CdCl_2$–$PbCl_2$ system. An exothermic enthalpy of mixing is expected to be associated with this result. The enthalpy data of Figure 1 indicate small negative deviations from ideality, a trend also reported by Bloom and Tricklebank (*1*).

The enthalpy measurements may be used to compute molar heat capacities. Assuming that the effect of the change in pressure is negligible, C_p was computed from the slope of the curves of enthalpy *vs.* temperature. The results are summarized in Table V and compared with those of Bloom and Tricklebank (*1*), Kelley (*6*), and Topol and Ransom (*11*). The latter work was limited to a temperature range 60° to 100° K. above and below the melting point of $CdCl_2$. The range of possible error must be increased for the C_p values, since differences must be taken in the calorimetric values and temperatures in determining slopes.

The error in C_p was taken as 3%, double that of the enthalpy values. The values agree well with those suggested by Kelley (*6*) and with the value for liquid $CdCl_2$ reported by Topol and Ransom (*11*). The values reported by them for solid $CdCl_2$ seems high which may account for their somewhat lower enthalpy of fusion. The agreement between these values and those of Bloom and Tricklebank (*1*) for solid $PbCl_2$ and $CdCl_2$ is satisfactory.

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Surface Tensions of Water–Methyl Ethyl Ketone Mixtures

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Surface tensions of water and methyl ethyl ketone mixtures are reported for concentrations from 0 to 10 weight % of methyl ethyl ketone and for temperatures from 20° to 60° C. The surface tensions, measured by the maximum bubble pressure method, were determined for use in analyzing boiling heat transfer data.

VARIOUS investigators discovered that the addition of certain volatile organic components to water affects the nucleate boiling process, especially the critical heat flux at which nucleate boiling fails and film boiling begins (*6*, *7*, *9*). Van Wijk, Vos, and von Stralen (*9*) experimented with several substances and found that methyl ethyl ketone (M.E.K.) increased the critical flux from heated wires by as much as 230%. Tests by Pitts and Leppert (*7*) also show an increase in the critical flux, but those of Owens (*6*) with larger diameter heaters did not show this effect. Leppert, Costello, and Hoglund (*5*) reported on nucleate boiling and observed the pronounced effect of additives on bubble size and frequency.

EXPERIMENTAL

Materials. The water was doubly distilled and the M.E.K. was Eastman Kodak reagent grade. Reagent grade M.E.K.

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Table I. Surface Tensions of Water–Methyl Ethyl Ketone Mixtures

Temp., °C.	Weight % M.E.K.	Surface Tension, Dyne/Cm.	Average Wt. %	$b(x_{av.})$, Dyne/Cm.
26.0	0.63	65.68		
26.2	0.63	65.36		
26.6	0.63	65.40		
26.6	0.63	65.36	0.67	69.27
37.2	0.71	63.74		
37.2	0.71	63.78		
37.5	0.71	63.90		
37.5	0.71	63.90		
26.8	1.17	61.89		
26.8	1.17	61.77		
27.0	1.17	61.61		
27.0	1.17	61.53		
38.3	1.17	59.84		
38.4	1.17	59.87		
38.5	1.17	59.80	1.19	65.62
38.5	1.17	59.72		
57.0	1.23	57.47		
57.0	1.23	57.47		
57.1	1.23	57.55		
57.1	1.23	57.55		
57.1	1.23	57.62		
22.4	1.95	57.07		
22.4	1.95	57.07		
22.4	1.95	56.68		
22.6	1.95	56.84		
22.6	1.95	56.64		
29.5	2.01	55.65		
29.5	2.01	55.65		
29.6	2.01	55.97		
29.6	2.01	56.05	1.96	60.37
40.7	1.95	54.47		
40.7	1.95	54.55		
40.6	1.95	54.59		
40.5	1.95	54.59		
50.9	1.95	53.48		
50.9	1.95	53.52		
50.9	1.95	53.48		
50.9	1.95	53.36		
27.1	4.12	49.77		
27.1	4.12	49.73		
27.1	4.12	49.77		
27.1	4.12	49.73		
39.3	4.06	47.99		
39.4	4.06	47.95	4.08	53.79
39.6	4.06	47.99		
40.0	4.06	47.95		
57.4	4.06	45.51		
57.4	4.06	45.63		
57.4	4.06	45.55		
57.4	4.06	45.67		
22.6	6.06	46.06		
22.5	6.06	46.06		
22.5	6.06	46.02		
22.5	6.06	45.98		
22.6	6.06	46.34		
29.4	6.06	45.11		
29.4	6.06	45.11		
29.4	6.06	45.07		
29.5	6.06	45.07	6.04	49.50
40.0	6.12	43.57		
40.0	6.12	43.65		
40.0	6.12	43.65		
40.0	6.12	43.61		
50.9	5.90	42.47		
50.9	5.90	42.51		
50.9	5.90	42.43		
50.9	5.90	42.51		
19.5	9.56	40.38		
19.5	9.56	40.26		
19.5	9.56	40.50		
19.6	9.56	40.46		
19.6	9.56	40.46		
29.5	9.76	38.52		
29.5	9.76	38.56		
29.5	9.76	38.60		
29.5	9.76	38.56	9.63	42.91
39.7	9.56	37.42		
39.7	9.56	37.57		
39.7	9.56	37.57		
39.7	9.56	37.56		
51.0	9.66	34.61		
51.0	9.66	34.85		
51.1	9.66	34.85		
51.1	9.66	34.85		

was selected because interest in the effects of this additive stemmed primarily from possible engineering applications. More highly purified M.E.K. would have been of equal or greater scientific interest but not of practical importance to this investigation. Measured values of n_D^{25} for the water and M.E.K. used were 1.3325 and 1.3768, respectively.

Concentrations. Concentrations of the individual samples were obtained by measuring their refractive indices at 25° C. The precision of this measurement was approximately ±0.1% M.E.K. The final value of the concentration for each solution was the average value derived from several n_D^{25} measurements on the given solution. The variation of n_D^{25} with weight per cent was obtained from published data (*8*) and was checked by measuring the refractive indices of weighed samples.

Surface Tension. Surface tension was measured by the maximum bubble pressure method (*1*) using a single capillary tube and a mercury aspirator. The tube used was drawn from precision-bore capillary tubing and was broken at a right angle to the tube axis. The radius of this capillary tip was measured from pictures taken at a magnification of 1300 and was 0.003169 cm. with a deviation of less than 1% in any direction. Temperatures of the solutions were measured with a mercury thermometer with an accuracy of ±0.1° C.

RESULTS AND DISCUSSION

Before measuring the surface tensions of the solutions the apparatus and procedures were checked out by measuring the surface tension of pure water. Fifteen runs with pure water from 20° to 60° C. gave a standard deviation from published values (*2*) of ±0.19 dyne per cm. or ±0.27% at 40° C.

Although the surface tension of pure M.E.K. was not of primary interest, measurements were made at 26° and 39° C. The respective measured values were 4 and 0.5% higher than the published values (*3*). The cause of this experimental discrepancy was not determined.

The experimentally determined mixture surface tensions are given in Table I as a function of concentration (weight per cent M.E.K.) and temperature, ° C. For all concentrations and temperatures, the data can be represented within the experimental accuracy by a straight line:

$$\gamma(x, t) = b(x) - 0.1452\, t \qquad (1)$$

where γ is the mixture surface tension in dynes per centimeter, t is the temperature in ° C., x is the mixture concentration in weight per cent of M.E.K., and b is the value of γ at $t = 0°$ C. as determined by a least squares analysis of the experimental data.

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%.