the mean ionic activity of HCl and consequently increases P_{HCl}. On the other hand, addition of HCl to the system decreases the activity of water molecules and hence reduces the partial vapor pressure of water. The existence of a minimum point on the plot of log P_t *vs.* HCl concentration shows a negative deviation from Raoult's law.

Experimental data obtained at 70° C. are correlated by the following equation with an average absolute deviation of 12.1%. Details of the derivation are deposited with the Americal Society for Information Science.

$$\log\left[\frac{P_{HCl}}{P_t - P_{HCl}} \times \frac{x_3(2x_1 + 3x_2 + x_3)}{x_1(x_1 + 2x_2)}\right] = 21.94\ (x_1 + 3x_2)^{4/3} - 0.93$$

where x_1, x_2, and x_3 are mole fractions of HCl, $FeCl_2$, and H_2O in the solution, respectively.

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Measurement of Contact Angles Encountered during Distillation of Binary Liquids on a Copper Surface

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Contact angles are presented for the systems methanol-water, *n*-heptane–methylcyclohexane, acetone-water, *n*-heptane–toluene, benzene-cyclohexane, ethanol-water, 1-propanol–water, and benzene–*n*-heptane in contact with a copper surface, measured under conditions of distillation both at total reflux and at equilibrium.

A CONSIDERABLE amount of published data exists listing angles of liquids in contact with a variety of solid surfaces measured over a range of temperatures in the presence of air or saturated vapor-air mixtures. However, only scant information is available in the literature (*2, 3, 4*) where contact angles have been measured under conditions which are most frequently encountered in chemical engineering operations—namely, distillation, absorption, or heat transfer. The systems examined in this investigation are of commercial importance, and the difficulty of separation by distillation has been attributed generally to the reduction of surface area produced by the changes in surface properties (*5*). When a liquid mixture is distilled, the liquid and vapor exchange may cause an increase or decrease in the surface tension. For some systems these changes can be significant, and the performance of a packed distillation column is influenced considerably by these changes. A system is declared to be positive if its surface tension value increases down the column and negative if the value decreases. A decrease in surface tension will enhance the wetting of a packing, while an increase in surface tension results in a reduction of the effective wetted area.

The determination of the contact angles now presented is of prime importance in understanding the role of surface properties on transport in packed columns.

EXPERIMENTAL

The designs of apparatus employed for determining the contact angles are shown in Figures 1 and 2, and are developments of designs described previously by Ponter *et al.* (*2*).

Contact Angle for Liquids in Equilibrium with Their Surrounding Vapor. The apparatus shown in Figure 1 consisted essentially of a 1-liter flask, an observation cell, and a cold finger condenser. The flask was fitted with a thermometer pocket and a condensate return line, and was heated with a 300-watt Isomantle. The observation cell (15 cm. × 10 cm. o.d.) comprised two sections, the lower section being fitted with two optical flats situated on opposite sides of the cell. The copper plate was supported by the glass structure above the central vapor line from the flask. The upper section was fitted with a thermometer pocket, a vapor exit line to the condenser, and a hollow rubber plug to allow the introduction of a sessile drop via a hypodermic needle. The cell sections were fitted with electrical heaters and lagged with asbestos to minimize heat losses.

The copper surface was carefully prepared by polishing to a surface roughness of 6 microns, degreasing, and finally washing in the fluid under test, before being introduced to the cell. Care was taken to ensure that the plate was horizontal. To achieve this, the vertical cross wire in the travelling microscope was aligned against a thin plumb line. The goniometer eyepiece was then rotated through 90° and the specimen plate adjusted until its surface lay parallel to the new position of the cross wire. Variations of plate inclination of up to ½ degree to the horizontal did not affect the value of contact angle obtained. A period of 3 hours was then allowed for the system to come to

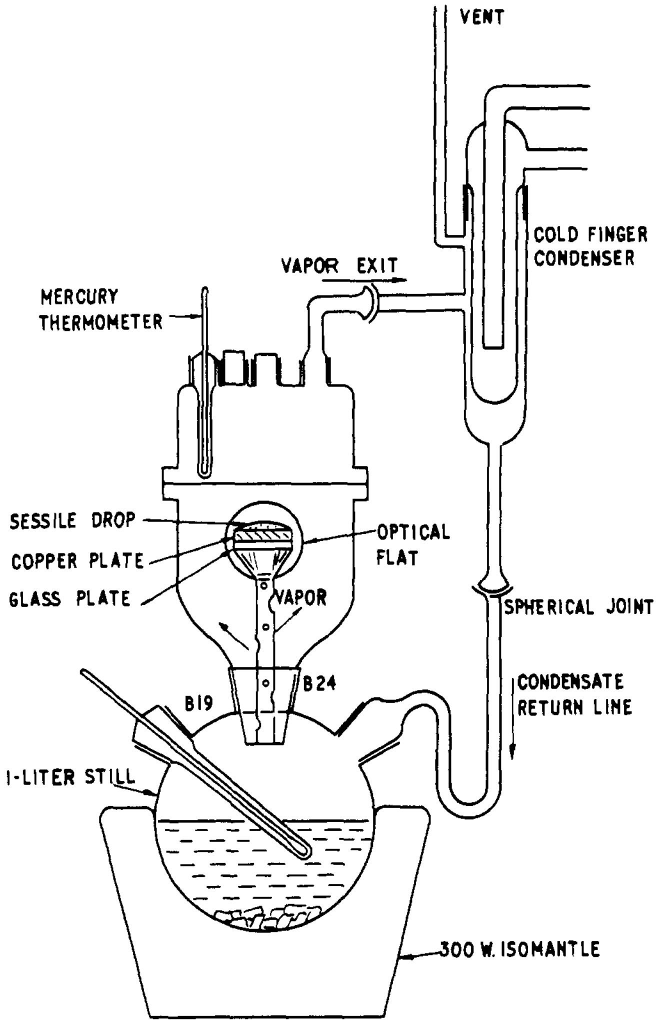

Figure 1. Apparatus employed for contact angle measurement under equilibrium conditions

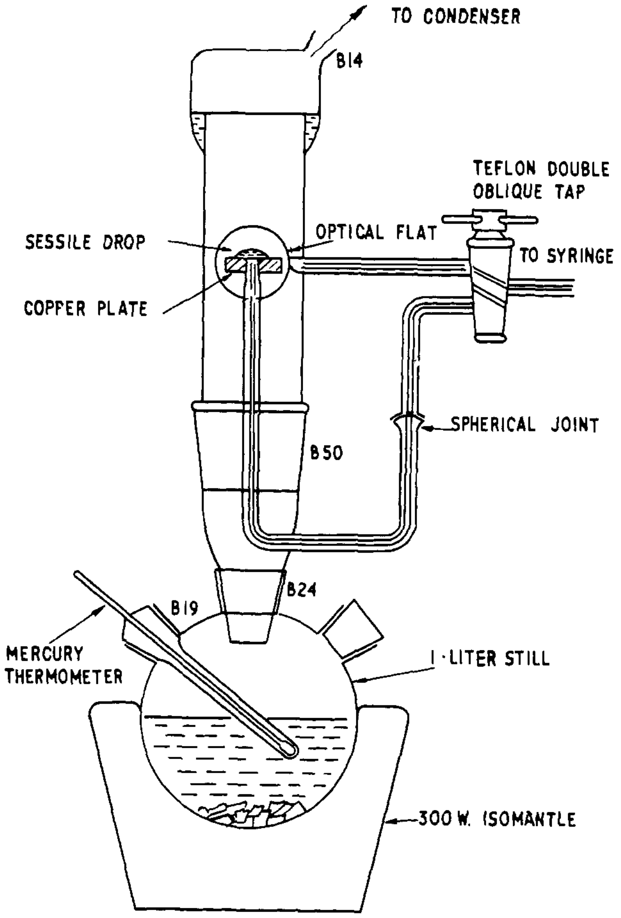

Figure 2. Apparatus employed for contact angle measurement under total reflux conditions

equilibrium, after which time a liquid sample was taken from the flask through the thermometer pocket via a hypodermic needle and introduced to form a sessile drop on the copper surface. Sufficient liquid must be introduced at this stage so that the equilibrium drop height is reached, this height being the maximum attainable—any addition to the drop only resulting in an increase in diameter. Padday (*1*) has shown that the equilibrium drop height, *h*, may be calculated from the equation

$$1 - \cos \theta = \frac{\rho g h^2}{2\gamma_{LV}} \tag{1}$$

This equation was derived assuming that for large drops the top surface becomes flat and the terms involving the curved rim can be neglected. The drop was allowed to come to equilibrium with its vapor, and the contact angle was measured by observation through a traveling microscope fitted with a goniometer eyepiece. The above procedure was repeated 5 times for one particular liquid composition and the average value taken. The values were reproducible to ±1%, and are given in Tables I and II.

Contact Angle for Liquids under Conditions Simulating Distillation at Total Reflux. The apparatus shown in Figure 2 was comprised of a 1-liter flask, a glass wetted-wall column (6-cm. diameter, 23-cm. length), and a condenser where vapor was condensed before returning to the column as a liquid film. The flask was heated using a 300-watt Isoman-

Table I. Contact Angles Measured under Equilibrium Conditions

System					
Positive below Azeotrope Negative above Azeotrope		Positive			
Ethanol/Water		*n*-Heptane/ Methylcyclohexane		Methanol/Water	
Mole % ethanol	Contact angle °	Mole % *n*-heptane	Contact angle °	Mole % methanol	Contact angle °
0.0	70.3	0.0	0.0	0.0	70.3
0.3	66.9	4.0	3.7	0.5	54.5
0.5	62.2	10.0	5.7	4.5	42.0
1.5	60.2	15.0	9.3	9.0	28.3
2.5	50.0	16.5	4.0	19.0	16.5
3.5	45.4	26.5	2.0	29.0	10.0
4.0	43.3	33.0	0.0	32.0	9.0
13.5	12.8	39.0	0.0	39.5	4.3
17.5	10.2	50.0	0.0	54.0	2.0
20.0	8.7	60.0	0.0	69.8	0.0
22.5	6.7	67.5	0.0	74.9	0.0
38.5	3.2	80.0	0.0	85.4	0.0
45.0	2.2	90.1	0.0	90.2	0.0
60.0	2.0	95.0	0.0	96.0	0.0
74.5	1.9	100.0	0.0		
79.0	1.0				
89.4	1.0				
96.2	0.3				
100.0	0.0				

tle. A 2-mm. i.d. glass sampling line was fitted to the column directly opposite to the copper plate. Samples withdrawn using a hypodermic needle were returned to the copper plate via the Teflon double-oblique tap. The 1-inch-square copper plate was fitted to the capillary tube using a neoprene O-ring (Figure 3). The optical flats and heaters were positioned as previously described, and again the copper plate was treated and leveled before allowing the apparatus to attain steady state.

A liquid sample was then withdrawn from the liquid film and carefully injected onto the copper surface, again ensuring that sufficient volume was present to maintain the equilibrium drop height. The period between placing the fluid on the surface and measuring the contact angle was always less than 3 seconds. The contact angles were again observed, the reported values being an average of 5 readings. The values were reproducible to ±1%, and are given in Tables III, IV, and V. Under these conditions, the contact angle measured and the composition of the drop surface will vary with time. The velocity of the vapor in the column controls the transfer rate to the drop, and so the boil-up rate and column diameter will have an effect

Table II. Contact Angles Measured under Equilibrium Conditions

System					
Negative		Positive		Positive below Azeotrope Negative above Azeotrope	
n-Heptane/Benzene		Acetone/Water		1-Propanol/Water	
Mole % benzene	Contact angle °	Mole % acetone	Contact angle °	Mole % 1-propanol	Contact angle °
0.0	0.0	0.0	70.3	0.0	70.3
5.0	0.5	1.5	49.9	0.5	23.5
12.0	1.0	7.5	39.8	5.0	9.0
16.0	2.0	13.5	33.0	10.0	4.0
28.0	6.2	16.0	31.3	20.1	2.0
40.0	10.0	30.0	20.0	39.7	1.0
50.0	9.5	45.0	10.0	84.9	0.0
68.0	10.0	55.0	6.7	90.0	0.0
68.5	12.0	80.0	0.0	95.0	0.0
78.0	11.5	90.0	0.0		
93.2	9.2	95.0	0.0		
97.0	4.5	100.0	0.0		
99.0	1.0				

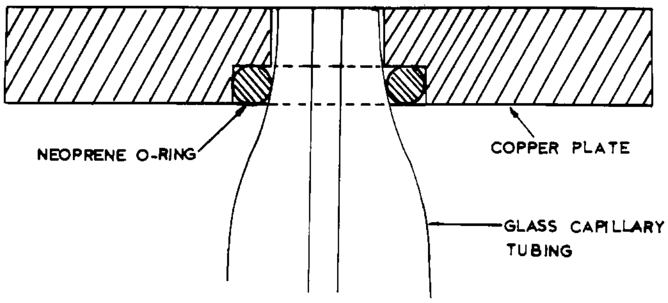

Figure 3. Copper plate assembly

Table III. Contact Angles Measured under Total Reflux Conditions

System					
Negative below Azeotrope Positive above Azeotrope		Positive			
Benzene/ Cyclohexane		Ethanol/ Water		*n*-Heptane/ Methylcyclohexane	
Mole % benzene	Contact angle °	Mole % ethanol	Contact angle °	Mole % heptane	Contact angle °
0.5	6.0	0.0	72.9	0.0	0.0
1.0	10.0	4.5	61.6	1.0	0.0
7.6	11.5	14.0	36.4	5.2	2.0
18.0	12.5	16.5	38.0	10.0	1.0
29.5	14.0	17.0	28.5	13.2	0.7
47.0	11.0	34.0	5.0	20.0	0.0
48.5	4.5	60.2	0.0	30.0	0.0
54.0	2.5	70.5	0.0	40.0	0.0
63.5	0.0	79.5	0.0	50.1	0.0
82.0	0.0	87.5	0.0	60.0	0.0
96.0	2.5	92.0	6.0	70.0	0.0
98.0	4.0	95.0	8.0	80.2	0.0
		97.5	7.8	90.0	0.0
		100.0	0.0	95.0	0.0
				100.0	0.0

Table IV. Contact Angles Measured under Total Reflux Conditions

System					
Positive		Negative		Positive	
Methanol/Water		*n*-Heptane/Benzene		Acetone/Water	
Mole % methanol	Contact angle °	Mole % benzene	Contact angle °	Mole % acetone	Contact angle °
0.0	72.9	0.0	0.0	0.0	72.9
1.0	56.0	14.0	2.3	11.5	55.2
2.5	25.5	24.0	11.0	24.0	28.5
8.4	17.3	25.0	10.0	36.0	28.5
12.2	11.0	37.5	10.2	53.4	12.6
21.0	5.6	48.5	11.0	67.5	6.1
30.5	2.0	54.5	11.1	83.5	1.0
60.0	0.0	59.0	11.9	87.5	0.0
67.8	0.0	73.5	11.0	89.0	0.0
78.2	0.0	74.0	10.9	91.2	0.0
86.3	0.0	76.5	11.5	95.1	0.0
90.2	0.0	88.0	11.2	99.0	0.0
96.0	0.0	94.0	10.8		
100.0	0.0	99.4	1.2		

Table V. Contact Angles Measured under Total Reflux Conditions

System			
Positive below Azeotrope Negative above Azeotrope		Positive	
1-Propanol/Water		*n*-Heptane/Toluene	
Mole % 1-propanol	Contact angle °	Mole % *n*-heptane	Contact angle °
0.0	72.9	0.0	5.0
0.5	40.0	4.0	1.5
1.0	34.7	5.0	1.0
4.6	16.2	10.0	0.0
10.0	9.9	21.0	0.0
24.2	10.0	37.0	0.0
25.0	0.0	69.0	0.0
35.2	0.0	95.0	0.0
40.0	0.0	99.0	0.0
41.7	0.0		
45.1	11.5		
55.0	12.5		
62.5	12.8		
72.4	10.5		
81.9	6.0		
100.0	0.0		

on θ. However, in these experiments, approximately constant boil-up rates were maintained. To be completely quantitative, the contact angle should be determined at a specific vapor velocity.

DISCUSSION

An interesting phenomenon was observed while measuring the contact angles under conditions of mass transfer for the fluids under test. For all the positive systems studied, the sessile drop remained immobile, with no indication of interfacial turbulence occurring at any stage in the experimental procedure. However, for the negative systems, a considerable amount of agitation was evident in the droplet, which resulted at some concentrations in the production of droplets ejected from the main sessile body. This phenomenon explains why distillation efficiencies are often high for negative systems, although the contact angle would suggest a poor wetting performance and hence low transfer area. The behavior has an analogy in liquid-liquid extraction, where systems with negative interfacial tensions produce satellite droplets.

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NOMENCLATURE

ρ = density of sessile drop
g = acceleration due to gravity
h = equilibrium drop height
γ = surface tension
θ = contact angle

Subscripts

L = liquid
V = vapor

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Low-Temperature Volumetric Properties of Methane

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Pressure and temperature measurements were performed on 16 constant-mass methane samples ranging in density from 0.04 to 0.36 gram per cc. for temperatures between 150° and 273° K. at pressures to 680 atm. Saturation temperatures, pressures, and densities were also measured. Analysis of the data in the critical region suggested critical constants of 190.77° K., 45.66 atm., and 0.1625 gram per cc. An empirical equation of state was developed for the isochoric data which reproduces the measured pressures with an average error of 0.02% and a maximum error of 0.08%. Certain qualitative features of the isochoric equation representing the volumetric behavior of methane are discussed.

THE pressure-volume-temperature relations for methane were determined as part of a continuing program to investigate the basic properties of gases and liquids at low temperatures. Data have been recently reviewed and reported for hydrogen and methane in the gas phase (*14*, *15*), helium and nitrogen in the gas phase (*4*, *5*), and low-density methane (*8*, *9*). Available data sources for the properties of pure methane are numerous, but they are in serious disagreement, especially in the temperature region below 0° C. A recent compilation by Din (*6*) summarizes many of the discrepancies and deficiencies of the data.

Three significant investigations have been carried out on methane gas in the temperature range below 0° C. The earliest was by Kvalnes and Gaddy (*12*) in 1931 at temperatures to −70° C. and pressures to 1000 atm. Measurements by Mueller *et al.* (*14*, *15*) extended the data to −128.7° C. and 510 atm. Both of these investigations claimed compressibility factors accurate to 0.1%; however, in some regions disagreements between the two sets of data are as large as 2 or 3%. Hoover *et al.* (*8*, *9*) measured virial coefficients and gaseous compressibility factors between 131° and 273° K. at pressures to 40 atm.

Investigations at temperatures above 0° C. were conducted by Michels and Nederbragt (*13*), Schamp *et al.* (*16*), and Douslin *et al.* (*7*). The results of all these measurements above 0° C. are in close agreement. The results reported here agree with those of Douslin *et al.* within 0.03% at 0° C.

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