Vapor Liquid Equilibria up to 100 MPa: A New Apparatus

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A new static cell for vapor-liquid equilibria up to 100 MPa between 233 and 433 K is presented. A detachable sampling microcell and a special chromatographic injector are used in a new sampling system suitable for gas chromatographic analysis of mixtures with high boiling components. The test system is N_2—n-Heptane at 305.45 K.

SCOPE

Vapor-liquid partition coefficients at high pressures up to 100 MPa are needed for direct industrial applications especially in oil recovery and for establishing methods of calculation, for instance providing parameters in mixing rules. P, T, x, y data are needed especially for mixtures of hydrocarbons of various molecular weight (as high as possible) and families (aromatics, paraffins, cycloalkanes) with gases (N_2, CO_2, H_2S, CH_4).

Few experimental methods have been developed. Alwani and Schneider (1969), Lentz (1969), Engels and Schneider (1979) obtain P, V, T data only, while Krichevsky and Gamburg (1942) measure P, T, y data. Among apparatuses leading to P, T, x, y, measurements, there are the dynamic apparatus of Michels et al. (1950) (pressures up to about 80 MPa) and the static one of Akers (1954) (pressures up to about 70 MPa).

At high pressures, the main experimental difficulty is sampling. The systems proposed by Yarborough and Vogel (1967), Jacoby and Tracht (1975), Dorokhov et al. (1972) are not very satisfactory, because the amount of withdrawn samples is too important, the sampling system is very complicated, or compounds with boiling point above equilibrium temperature cannot be analyzed.

The experimental method described here is reliable, and relatively simple. It allows measurement between 233 and 433 K and from 5 to 100 MPa. The original sampling method with sampling microcell which can be taken apart from the equilibrium cell to the special chromatographic injection port, allows measurement with heavy hydrocarbons which need to be heated above the equilibrium temperature for complete vaporization.

CONCLUSIONS AND SIGNIFICANCE

The static method described here has been tested and found reliable for measurements of vapor liquid equilibria of N_2—n-Heptane system at 305.45 K and from 1 to 100 MPa.

Reproduction of mole fraction determinations is within 0.003.

The method can be applied in the same range of pressures and temperatures to determine vapor-liquid equilibria for systems of gas and heavy hydrocarbons, similar to those encountered in oil fields.

Vapor liquid equilibria have been measured at high pressures by dynamic and static methods. Dynamic methods use a biphasic continuous flow of coexisting phases to achieve mass transfer of components until equilibrium is reached. The phases should then be continuously separated without perturbing the equilibrium. This requires sophisticated electronic regulations. In static methods, the gas-liquid mixture is simply stirred in a closed cell until pressure and temperature reach equilibrium values, then samples of both phases are withdrawn and analyzed. If sampling can be achieved in a simple and reproducible way, static methods offer a better chance to achieve the least expensive, accurate laboratory apparatus.

EXPERIMENTAL METHOD AND APPARATUS

The experimental setup is represented in Figure 1. It consists of three parts:

- the equilibrium cell placed in thermostat AT and equipped with detachable sampling microcells;
- the feed assembly used to fill the equilibrium cell with the liquid

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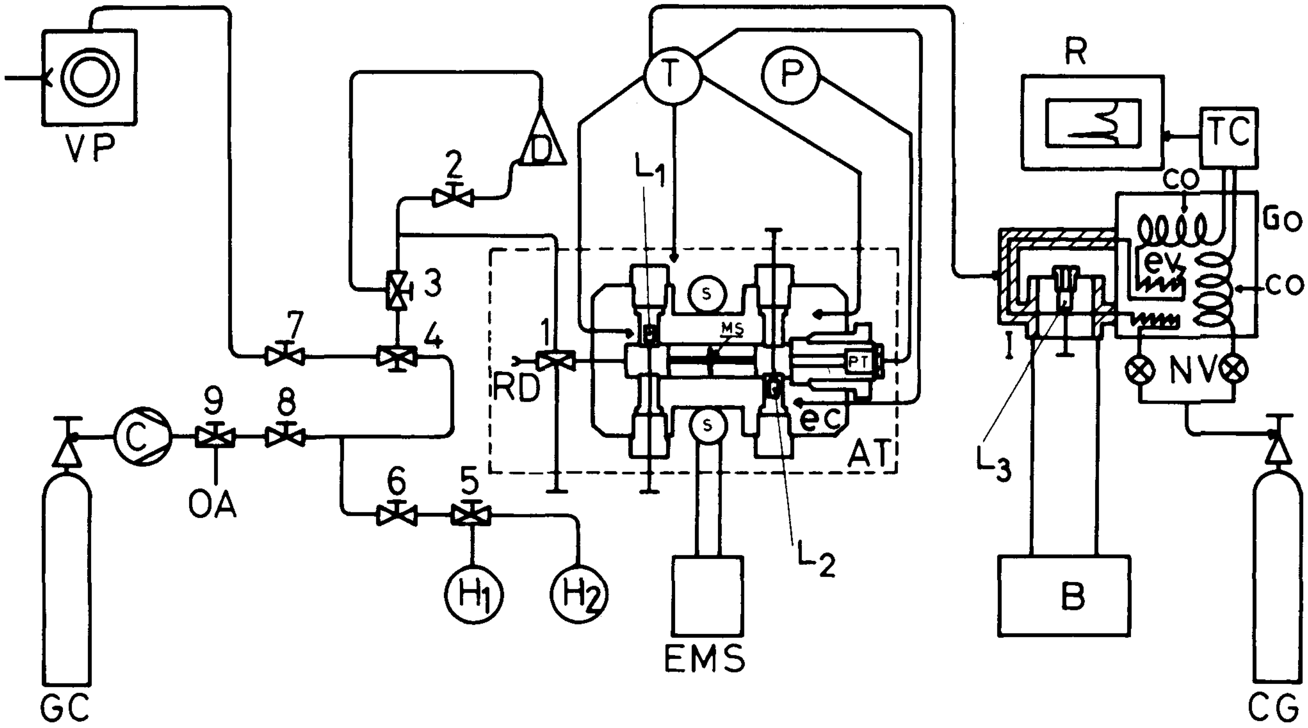

Figure 1. General setup of the apparatus.

AT	Air thermostat
B	Temperature controller for the injection port
C	Compressor
CG	Carrier gas for GLC
CO	GLC columns
D	Degassing cell
EC	Equilibrium cell
EMS	Power supply for solenoids
EV	Expansion volume playing a role of pressure regulator
GC	Gas cylinder (gaseous component of the mixture)
GO	Gas chromatograph oven
H_1	HEISE gauge manometer (60 MPa)
H_2	HEISE gauge manometer (100 MPa)
I	Injection port assembly
L_1, L_2, L_3	Sampling microcell holes
MS	Magnetic stirrer
NV	Needle valves
OA	Outlet to atmosphere
P	Electronic read out for pressure
PT	Pressure transducer
R	Recorder
RD	Rupture disc
S	Solenoid
T	Temperature measurement
TC	Thermal conductivity detector
VP	Vacuum pump
⋈	(1 . . . 9) shut-off valves

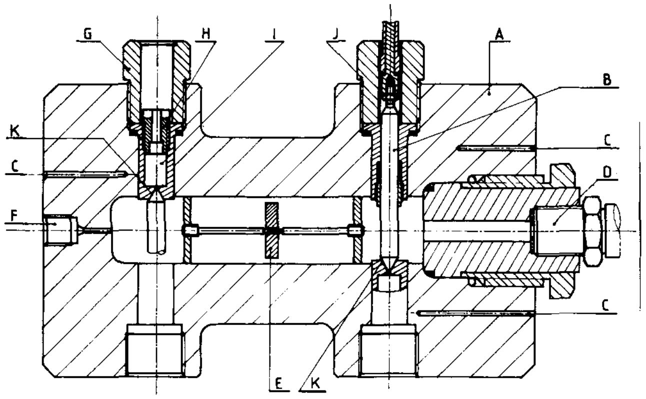

Figure 2. Equilibrium cell.

A	Cell body
B	Sampling valve with packing joint
C	Thermocouple well
D	Pressure transducer
E	Magnetic stirrer
F	Connection to filling circuit
G	Microcell bearer fixing-pin
H	Microcell set-screw
I	Microcell
J	Valve fixing-pin
K	Seat of sampling valve stem

component degassed in cell D and the gaseous component through a compressor,

- the analysis setup: a gas-liquid chromatograph with special injection port.

The equilibrium cell is drawn in Figure 2. It is made of stainless steel (XN 26 TW from AUBERT and DUVAL, AFNOR E-Z6-NCT-25). Its internal capacity is 100 cm^3. The two holes, drilled in the two opposite faces along the axis of the cell, receive the pressure transducer D and the feed line F. The two holes drilled through diameters of the cell are designed to receive each on one side of the cell the mechanism of valve B and on the other side the seat K of the stem of valve B and a sampling microcell I. Valve B's have nonrotating stems packed below the threads, because it was found necessary to achieve a reliable leakproof seal using a soft metal deposited on the conical part of the stem.

Other seals are made with Viton O-rings except for the connection of the pressure transducer to the cell (Teflon gasket) and the connection of the feed line (Autoclave Engineers high pressure connection). Efficient stirring is obtained with a permanent magnet rotating in a magnetic field induced by four solenoids located outside the cell (S in Figure 1).

Temperature is kept constant within 0.25 K by the air thermostat which was preferred to a liquid bath because the temperature range would have required two different liquids and it would have been impossible to clean the microcells before analysis. Thermal equilibrium is checked by the indications of thermocouples placed in several parts of the cell. The thermocouples (K type iron — constantan) are connected to a digital display T (Fluke 2100). They are calibrated against Brooklyn mercury thermometers (accuracy 0.05 K); the accuracy of the thermocouples is evaluated to 0.1 K. Pressure is measured inside the equilibrium cell by a transducer (BLH, type GPH 0-138 MPa) connected to an electronic readout *P* (BLH, type 450), Figure 1.

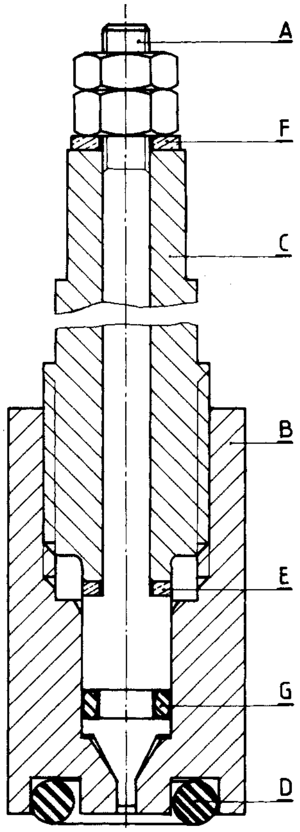

Figure 3. Sampling microcell.

A	Stem
B	Microcell body
C	Driving screw
D,G	Joints
E,F	Antifriction rings

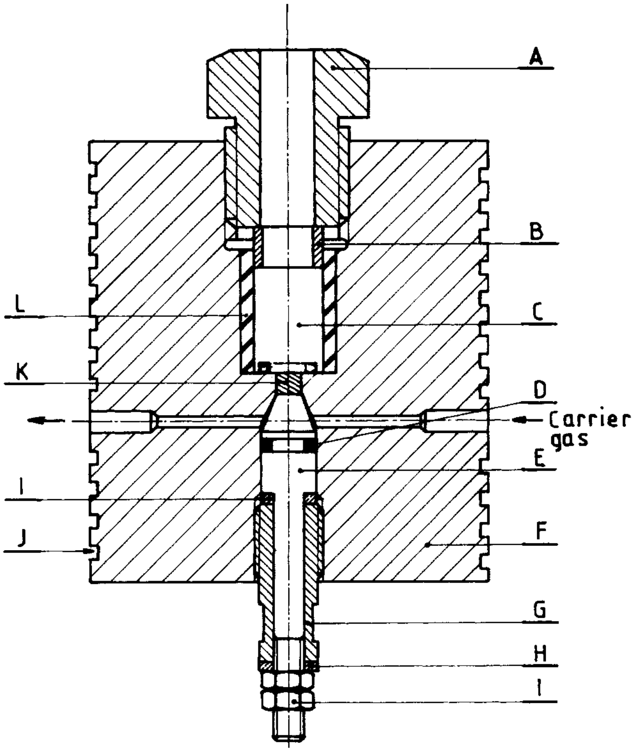

Figure 4. Injection port assembly.

A	Hold-down nut
B	Hold-down ring
C	Microcell seating
D	Joint
E	Stem axis
F	Body of the injection port assembly
G	Driving screw
H	Antifriction ring
I	Nut
J	Heating resistance fixing-groove
K	Sample Expansion volume
L	Thermal shield

Pressure transducer is calibrated at each working temperature against two BOURDON type manometers (HEISE), with accuracy of 25 KPa up to 60 MPa and 50 KPa at higher values. Both manometers are periodically calibrated against a dead weight gauge balance (BUDENBERG type 280 H) with a working range from 1 to 110 MPa and an accuracy: 10^{-4} of full scale. The dead weight balance is associated to a null differential pressure transducer and indicator (RUSKA model 2413-705 and model 2416-708) of maximum sensitivity 1 Pa.

Sampling is the most original and the most critical part of the method. A good analysis of high boiling liquids requires heating the sample at a temperature which can be higher than equilibrium temperature before its introduction in chromatograph carrier gas. Heating the sample in a container in contact with the cell is impossible without perturbing the thermal equilibrium. Therefore, we use a sampling microcell which can be detached from the cell after filling it and transferred to a specially designed chromatographic injection port.

The sampling microcell represented in Figure 3 is designed to trap a sample of volume 15 μL between the conical part of the nonrotating stem A and the body of the cell in a space limited by O ring, G. The other O ring D, insures a leakproof seal when the sampling microcell is positioned in the equilibrium cell or in the injection port of the chromatograph.

Figure 4 represents the injection port. The sampling microcell can be placed in the hole C with its seating pressed against the bottom of the hole. An empty space *K* is left between the microcell seating and the conical part of the stem E of the injector valve. The whole injection port assembly can be heated by the resistor wound in the groove J. The thermal shield L around the microcell prevents extremely fast raise of temperature in the sampling microcell, before the sample is expanded into the empty space *K* when opening the valve of the microcell.

The experimental procedure starts with calibration of the pressure transducer at the chosen equilibrium temperature and calibration of the chromatograph equipped with thermal conductivity detectors (GIRDEL, model 30) using pure components. Then, the equilibrium cell is partially filled with the degassed liquid component at room temperature. Degassing of liquids is achieved by the method of Battino et al. (1971) in flask D of Figure 1. Gas from the cylinder GC is introduced into the cell through valves 9,8,4,3, until a pressure of 1 MPa is reached in the cell. Then valve 1 is closed, temperature is stabilized at the chosen value, pressure is raised by introducing the gaseous component using the compressor C (Nova Swiss). Magnetic stirring is started.

Pressure equilibrium is reached within 10 minutes of stirring. The sampling procedure is initiated. Microcells are introduced in holes L_1 and L_2 (Figure 1) to take vapor and liquid samples. They reach the cell temperature after a few minutes. Microcell and sampling valves, B (Figure 2) are open in this order. When they are closed again, after a few minutes, the sampling microcells can be taken apart using a special tool to operate from outside the thermostat.

This sampling method is simple and fast, because no displacement fluid like mercury or circulation pump are needed. The expansion of the fluid into the valve is very small in amplitude; it represents 5.10^{-4} in relative value of volume and it results in no observable effect on the sample reproducibility, because the dead volume between the equilibrium cell and the sampling microcell is small (4 μL). Microcell is transported to the chromatograph injector. One microcell and its thermal shield are introduced into the heated injection port assembly and sealed at the bottom by O ring D, tightened by screwing the nut A (Figure 4). Injection port valve E is opened for a short time to sweep the air from space *K* before expanding the sample by opening the microcell valve. When the whole sample is vaporized, it is injected into the carrier gas flow of the chromatograph by opening the valve of the injector.

A complete isotherm is obtained by changing the total pressure by addition of gaseous component or release of vapor phase between each sampling. Sampling is reproduced several times (two to four) for each experimental point.

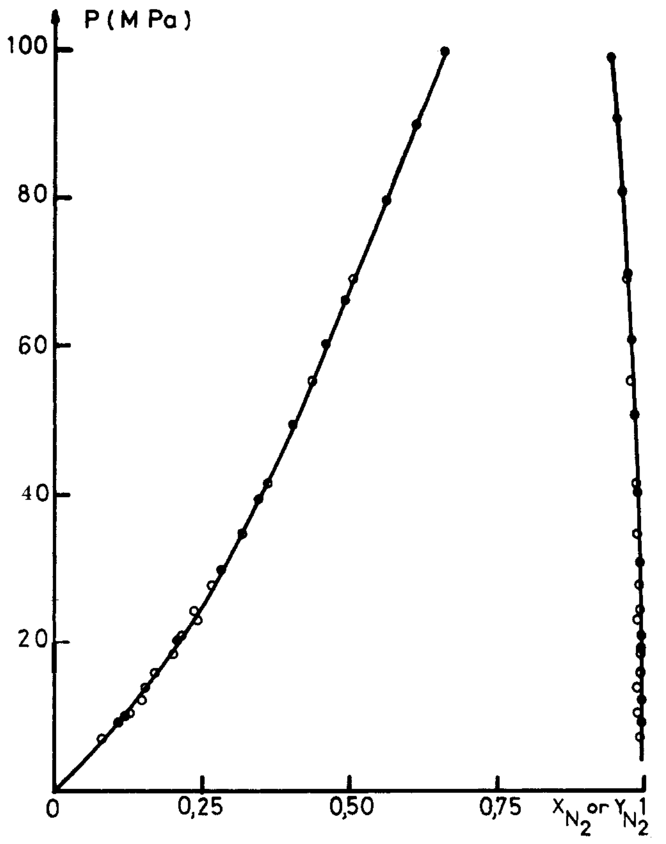

Figure 5. Pressure as a function of nitrogen mole fraction in nitrogen-n heptane system at 305.45 K.

● **Our results**

○ **AKER's results (1954)**

RESULTS AND DISCUSSION

Test mixture chosen was N_2-n-heptane already studied by Akers et al. (1954). Nitrogen is provided by *L'Air Liquide* with a certified purity of 99.9%. n-Heptane is supplied by Merck with a GLC-certified minimum purity of 99%. They were used without further purification.

Precision of analysis depends on chromatographic calibration (the pure samples introduced with a syringe for calibration are of the same order of magnitude as those introduced from the microcells) and reproducibility of sampling. Pressures are known within 0.1 MPa.

Our results (P, T, x, y) at $T = 305.45$ are reported in Table 1 and Figure 5 and compared with the data of Akers et al. (1954) at 305.35 K. In Table 1, K_i is obtained by interpolation of x_i or y_i on the P vs. x or y curves. Agreement between our results and literature values is within 0.005 in mole fraction. However, in the lower pressure range, the results of Akers et al. (1954) are a little more scattered.

Reproducibility was checked by analyzing two to four samples of each phase at the same pressure. The operation was repeated at many values of pressure. Maximum scatter is 0.003 in mole fractions. Different periods of time were tried for the sampling time during which the microcells are open on the equilibrium cell; no influence on the result of analysis was observed for time varying from a few seconds to one hour. The overall precision of our results including precision on chromatographic measurements and sampling reproducibility may be estimated at 0.01 for the liquid phase and 0.005 for the vapor phase.

TABLE 1. VAPOR-LIQUID EQUILIBRIUM DATA FOR N_2-n-HEPTANE SYSTEM AT T = 305.45 K.

P (MPa)	x_{N_2}	y_{N_2}	K_{N_2}	K_{nC_7}
9.1	0.10_7*	0.995_0	9.3_0	0.005_6
9.15	0.10_7*	0.995_0	9.3_0	0.005_6
9.2	0.109	0.995_2	9.1_3	0.005_4
9.2	0.106	0.995_2	9.3_9	0.005_4
9.2	0.111	0.995_2	8.9_6	0.005_4
10.05	0.118_8	0.99_5*	8.3_7	0.005_7
10.1	0.119_2	0.99_5*	8.3_5	0.005_7
19.1	0.20_0*	0.994_8	4.9_7	0.006_5
19.1	0.20_0*	0.994_8	4.9_7	0.006_5
19.1	0.20_0*	0.995_3	4.9_8	0.005_9
20.2	0.207_4	0.99_5*	4.8_0	0.006_3
29.75	0.285_0	0.99_3*	3.4_8	0.009_8
29.8	0.284_4	0.99_3*	3.4_9	0.009_8
29.8	0.281_2	0.99_3*	3.5_3	0.009_7
29.85	0.282_3	0.99_3*	3.5_2	0.009_8
30.7	0.29_0*	0.993_3	3.4_3	0.009_4
30.7	0.29_0*	0.992_8	3.4_2	0.001_0
30.7	0.29_0*	0.993_2	3.4_2	0.009_6
30.75	0.29_0*	0.992_8	3.4_2	0.001_0
39.4	0.346_6	0.98_9*	2.8_5	0.017
40.2	0.35_2*	0.989_7	2.8_1	0.016
40.2	0.35_2*	0.989_3	2.8_1	0.017
40.2	0.35_2*	0.989_3	2.8_1	0.017
40.25	0.35_2*	0.988_4	2.8_1	0.018
40.25	0.35_2*	0.988_4	2.8_1	0.018
49.3	0.406_7	0.98_5*	2.42	0.025
49.4	0.405_5	0.98_5*	2.43	0.025
50.7	0.41_1*	0.982_9	2.39	0.029
50.75	0.41_1*	0.983_7	2.39	0.028
50.75	0.41_1*	0.983_7	2.39	0.028
60.15	0.458_2	0.97_8*	2.13	0.041
60.25	0.460_4	0.97_8*	2.12	0.041
60.8	0.46_4*	0.978_5	2.11	0.040
60.85	0.46_4*	0.979_2	2.11	0.039
60.85	0.46_4*	0.978_0	2.11	0.041
65.9	0.491_9	0.97_5*	1.98	0.049
66.35	0.495_6	0.97_5*	1.97	0.050
66.5	0.495_2	0.97_5*	1.97	0.050
66.5	0.491_9	0.97_5*	1.98	0.049
69.55	0.50_8*	0.971_9	1.91	0.057
69.6	0.50_8*	0.974_0	1.92	0.053
69.8	0.50_9*	0.973_8	1.91	0.053
69.85	0.50_9*	0.969_9	1.91	0.061
79.6	0.564_4	0.96_5*	1.71	0.080
79.6	0.564_8	0.96_5*	1.71	0.080
79.75	0.561_8	0.96_5*	1.72	0.080
79.85	0.561_9	0.96_5*	1.72	0.080
80.85	0.56_5*	0.963_8	1.71	0.083
80.95	0.56_6*	0.962_5	1.70	0.086
81.0	0.56_6*	0.961_7	1.70	0.088
89.7	0.612_4	0.95_4*	1.56	0.119
89.9	0.613_4	0.95_4*	1.56	0.119
90.5	0.61_4*	0.952_0	1.55	0.124
90.6	0.61_5*	0.951_8	1.55	0.125
90.8	0.61_6*	0.952_7	1.55	0.123
99.1	0.65_7*	0.941_3	1.43	0.171
99.2	0.65_8*	0.942_4	1.43	0.168
99.25	0.65_9*	0.941_3	1.43	0.172
99.85	0.661_9	0.94_1*	1.42	0.175

* Smoothed values from experimental curves either $P = f(x_{N_2})$ or $P = f(y_{N_2})$.

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NOTATION

K_i = partition coefficient $(= y_i/x_i)$ for the component i
P = total pressure

T = temperature
x = liquid phase mole fraction
y = vapor phase mole fraction

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Liquid Film Flowing Slowly Down a Wavy Incline

A viscous lamina of given mean thickness flows down a wavy incline. Assuming low Reynolds number and small perturbations due to the wavy striations, the velocity profiles and the free surface profile are determined. It is found that the amplitude and phase shift of the free surface depend, in a complicated manner, on the surface tension and the wave length and orientation of the wavy striations. The motion of a particle on the free surface experiences drift which is also a function of the surface tension, the amplitude, wave length and orientation of the wavy incline.

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SCOPE

The flow of a liquid lamina down an inclined plane is important in many chemical engineering processes, e.g., film cooling, dip painting, swept film evaporators and vapor condensers. For low Reynolds numbers (less than about 5) the flow is smooth and laminar. Instability or ripples appear on the surface when the Reynolds number is larger than about 3 cosec α, where α is the inclination of the plate. The flow becomes turbulent when the Reynolds number is over 250. An excellent review of the theory and experiments on film flow was given by Fulford (1964).

The low Reynolds number flow down a smooth plate was first investigated by Hopf (1910) and Nusselt (1916). The velocity profile was a simple parabola. No theoretical or experimental work exists when the plate is not smooth but wavy, although some experiments show ridges or surface roughness increase turbulence at high Reynolds numbers (e.g. Laird et al 1962). The present paper studies the flow down a wavy or striated plate at low Reynolds numbers. The striations may be caused by wear, imperfect machining or they may be intentional as on textured surfaces. Particular emphasis is placed on the effect of striations on flow rate and on the lateral drift of the fluid when the direction of the striations is at an angle with the horizontal plane.

CONCLUSIONS AND SIGNIFICANCE

It is found, for a fixed mean depth of the film, the flow transverse to the striations is decreased in comparison to that of a smooth plate while the flow along the striations is increased. The decrease and increase of flow are not compensatory and depend on complicated functions of the wave length and a parameter D which includes the effect of the orientation of the striations and the surface tension. The fluid particles thus experience a drift (a tendency to flow in the direction of the striations). The mean drift angle increases with the amplitude of bottom striations. It decreases with increased wave length, inclination of the plate and surface tension. The striations on the inclined plate thus exert considerable influence on the transport properties of film flow.

The film flow over an inclined wavy plate, especially the three dimensional flow studied in the paper, has never been investigated before. It is hoped that the present work would lead to further discussion on this important topic, both experimentally and theoretically.

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