CHAPTER III

EXPERIMENT

A. Experimental Apparatus

1. Apparatus Description

The experimental unit was constructed earlier and has been in operation prior to this study. The bubble column (BC) and it's auxiliary equipment is shown in Figure 2. There are two columns made of borosilicate glass. The small column is 0.051 m in diameter and the large column is 0.229 m in diameter. Both columns are 3 m high. There are two separate storage tanks, one for each column. At the bottom of each column there are two flanges which hold the gas distributor plate (see Figure 3). Liquid and gas inlets are provided above and below the distributor plate, respectively.

Above each column there is an expansion unit which is connected to the gas-liquid separator. Entrained liquid can either be recirculated to the storage tank or discharged. The gas-liquid separator is connected to the scrubber which is filled with mineral spirits (varsol) in order to dissolve any wax vapors present in the gas. From the scrubber a vent line was provided to discharge gasses to the atmosphere.

The temperature in the column was monitored at the top and bottom of the column using two different thermocouples located inside the column. The column temperatures were controlled by two Omega CN2012 temperature controllers and monitored by an Omega model 199 multichannel temperature indicator. For other heated units, there were thermocouple ports which were connected to the temperature indicator. Temperature control in these units was achieved by

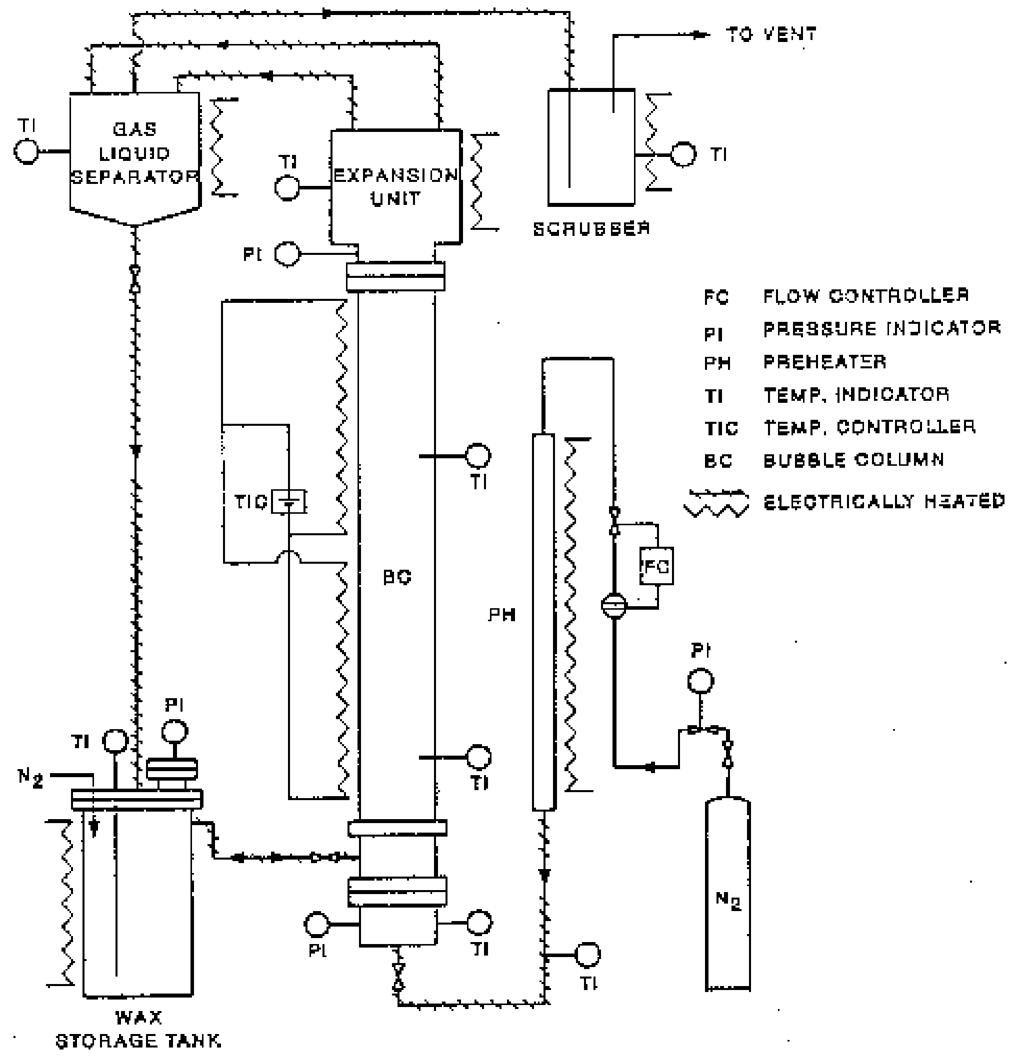


Figure 2. Flow diagram of experimental apparatus.

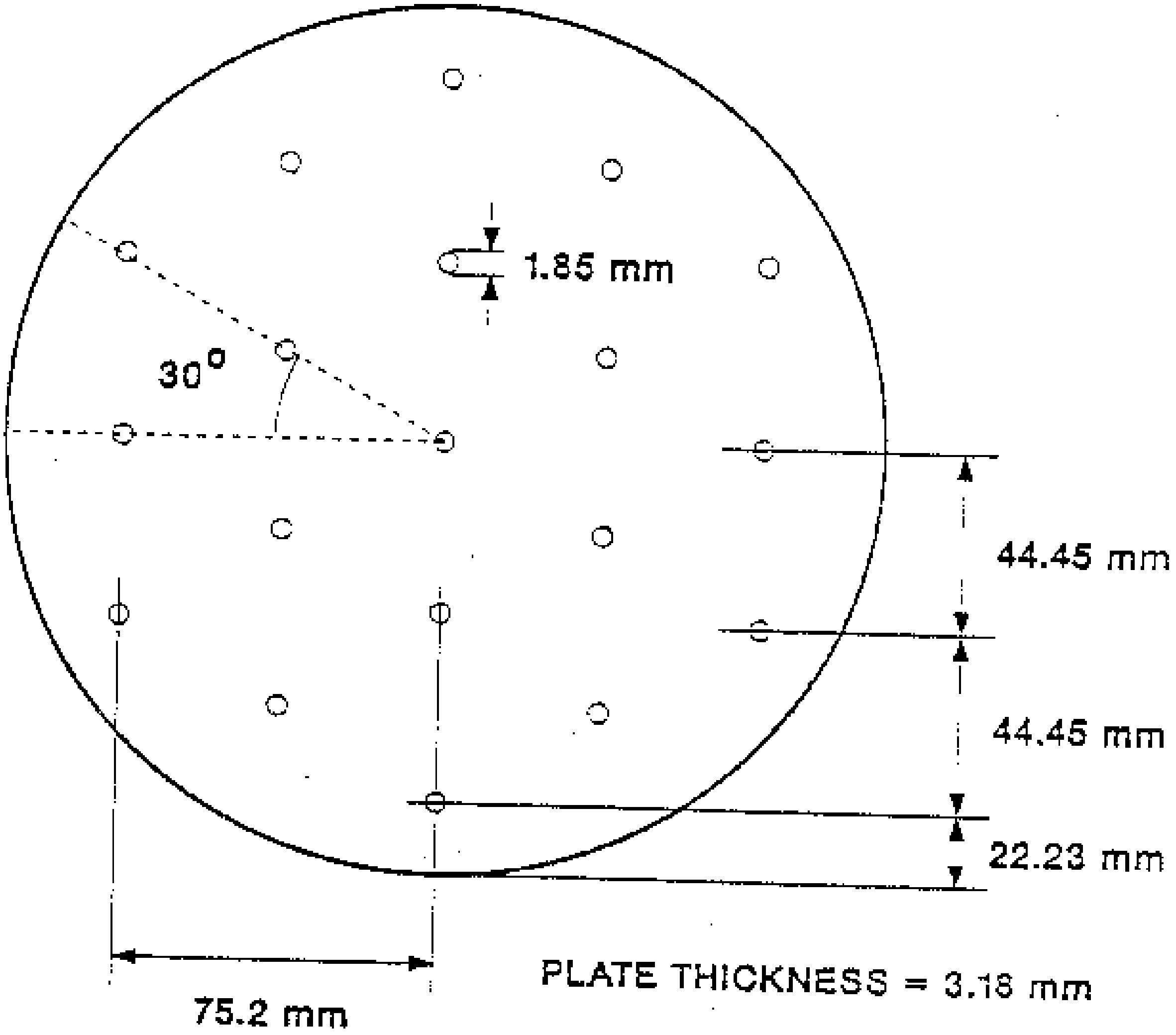


Figure 3. Sketch of 19x1.85 mm perforated plate distributor.

adjusting the variable voltage transformers which supplied power to each of these units. There were three ports on the side of the column which were used for differential pressure measurements: below the distributor, above the distributor, and at the top of the column.

2. Operation

Nitrogen from the cylinders was passed through the mass flow meter (FC) before it entered the preheater (PH)(electrically heated U shaped tube). The preheated gas entered the glass column (BC) through a gas sparger at the bottom of the column. Wax in the storage tank was heated to a temperature between 150 °C and 200 °C before it was transported to the column using a slight nitrogen overpressure. The column was preheated to a temperature of 150 °C before the wax was transferred to the column. The flow of nitrogen was maintained during the entire preheating period. The expansion unit, gas-liquid separator, scrubber and their connecting pipe lines were maintained at temperatures above the melting point of wax (~ 110 °C) to prevent solidification of any entrained liquid. The hot gasses leaving the separator passed through the scrubber before being vented to the atmosphere. For non-wax runs, the experimental operations were essentially the same as those for the hot-flow runs, except no heating was required.

B. Measurements of Average Gas Hold-up

Measurements

The average gas hold-up is defined as the volume percent of gas in the dispersion. A knowledge of the gas hold-up is essential for reactor design, because together with Sauter mean bubble diameter they determine the specific gas-liquid interfacial area available for mass transfer. Moreover, average gas hold-up allows estimation of residence time of gas in the reactor.

In this study, the work was divided into two parts:

1. Experiments with hot-molten waxes (paraffin wax; FT-200, and reactor waxes; Sasol and Mobil waxes), and a limited number of experiments with FT-300 wax. (Paraffin waxes (FT-200 wax and FT-300 wax) are purely synthetic polymers of CO and H_2 (mineral waxes). They are snow-white in color and absolutely free of residual oil and sulphur. When melted FT-waxes are fluid and water clear. Whereas, reactor waxes (Mobil wax and Sasol wax) are dark in color and contain residual oil and other compounds).
2. Experiments with non-wax liquids (distilled water, n-butanol, and aqueous solutions of n-butanol and carboxymethyl cellulose (CMC)).

The average gas hold up was measured by visual observation of the expanded height of the dispersion H_e (including any foam present) and the liquid static height (H_s), and its value was calculated from:

$$\epsilon_g = \frac{H_e - H_s}{H_e} \times 100 \tag{3.1}$$

1. Hot-Flow Runs

At a given set of operating conditions, a minimum of three readings of expanded height were recorded. For superficial gas velocities less than 0.05 m/s, readings were made after every thirty minutes, at higher gas velocities readings were made after every twenty minutes. The number of readings was increased whenever the observed height of foam increased with time until a steady height was attained. Before switching to another gas flow rate, the gas inlet supply was first cut off using an electromagnetic valve, then by closing gas inlet valve to avoid weeping of wax to below the distributor. The static liquid height was taken after all the gas bubbles had disengaged.

2. Cold-Flow Runs

The operating procedure for the cold-flow runs was basically the same as that for the hot-flow run, with the exceptions that no heating was done and running time was reduced to 50 minutes for each gas velocity (readings after 20, 20 and 10 minute intervals). The static height was maintained at about 2.0 m for most of the experiments. Static heights as low as 1 m were used in some of the experiments in the 0.051 m ID column with SMP distributor because of the presence of foam. A summary of different runs and operating conditions is shown in Table 3 for FT derived waxes and Tables 4 and 5 for non-wax mediums.

C. Measurements of Physical Properties

1. Fischer Tropsch Derived Waxes

The density and viscosity of the various waxes used in this study were measured at different temperatures to better understand the role of physical properties in determining the hydrodynamic properties of these waxes. It was not possible to measure the surface tension of the waxes and the literature value of this property was used. Physical properties obtained from measurements made in the present study are presented together with the existing literature data in Table 6.

Table 3. Details of Operating Variables for Runs With FT Derived Waxes.

Run number	Type of Wax	Temperature (°C)	Column ID (m)	Distributor type	Operating range of superficial gas velocity (m/s)
3-3	Sasol	265	0.229	19x1.85 mm PP	0.01-0.12
3-4	Sasol	200	0.229	19x1.85 mm PP	0.01-0.12
4-1	FT-300	265	0.229	5x1.00 mm PP	0.01-0.07
4-2	FT-300	170	0.229	5x1.00 mm PP	0.01-0.12
8-1	Sasol	265	0.051	1.85 mm orifice	0.01-0.12
8-2	Sasol	265	0.051	1.85 mm orifice	0.12-0.01
8-3	Sasol	200	0.051	1.85 mm orifice	0.01-0.12
8-4	Sasol	265	0.051	40 μm SMP	0.01-0.12
9-1	Mobil Composite Runs 9, 11 & 12	265	0.051	1.85 mm orifice	0.01-0.12
9-2	Mobil Composite Runs 9, 11 & 12	200	0.051	1.85 mm orifice	0.01-0.12
9-3	Mobil Composite Runs 9, 11 & 12	200	0.051	1.85 mm orifice	0.12-0.01
9-4	Mobil Composite Runs 9, 11 & 12	265	0.051	40 μm SMP	0.01-0.12
9-5	Mobil Composite Runs 4 & 7	265	0.051	1.85 mm orifice	0.01-0.12
9-6	Mobil Composite Runs 4 & 7	265	0.051	40 μm SMP	0.01-0.12
9-7	Mobil Composite Runs 4 & 7	265	0.051	1.00 mm orifice	0.01-0.12

Table 3. Continued

Run number	Type of Wax	Temperature (°C)	Column ID (m)	Distributor type	Operating range of superficial gas velocity (m/s)
9-8	Mobil Composite Runs 4 & 7	200	0.051	1.85 mm orifice	0.01-0.12
9-9	Mobil Composite Runs 5 & 8	265	0.051	40 μm SMP	0.01-0.12
9-10	Mobil Composite Runs 5 & 8	265	0.051	1.00 mm orifice	0.01-0.12
9-11	Mobil Composite Runs 5 & 8	265	0.051	1.85 mm orifice	0.01-0.12
9-12	Mobil Composite Runs 5 & 8	200	0.051	1.85 mm orifice	0.01-0.12
10-1	Sasol	265	0.051	40 μm SMP	0.01-0.12
11-1	FT-200	265	0.051	1.85 mm orifice	0.01-0.12
11-2	FT-200	200	0.051	1.85 mm orifice	0.01-0.12
11-3	FT-200	265	0.051	1.85 mm orifice	0.12-0.01
11-4	FT-200	200	0.051	1.85 mm orifice	0.01-0.12
11-5	FT-200	265	0.051	1.85 mm orifice	0.01-0.12
12-1	FT-200	200	0.051	1.85 mm orifice	0.01-0.12
12-2	FT-200	265	0.051	1.85 mm orifice	0.01-0.12
13-1	FT-300	265	0.051	1.85 mm orifice	0.01-0.12
13-2	FT-300	200	0.051	1.85 mm orifice	0.01-0.12
13-3	FT-300	265	0.051	1.85 mm orifice	0.12-0.01

Table 3. Continued

Run number	Type of Wax	Temperature (°C)	Column ID (m)	Distributor type	Operating range of superficial gas velocity (m/s)
14-1	FT-300	265	0.051	1.85 mm orifice	0.01-0.12
14-2	FT-300	265	0.051	1.85 mm orifice	0.12-0.01
15-1	FT-300	265	0.051	1.00 mm orifice	0.01-0.12
15-2	FT-300	265	0.051	1.00 mm orifice	0.12-0.01
16-1	FT-300	265	0.051	4.00 mm orifice	0.01-0.12
16-2	FT-300	265	0.051	4.00 mm orifice	0.12-0.01
17-1	FT-200	265	0.051	1.00 mm orifice	0.01-0.12
17-2	FT-200	265	0.051	1.00 mm orifice	0.12-0.01
18-1	FT-200	265	0.051	1.85 mm orifice	0.01-0.12
18-2	FT-200	265	0.051	1.85 mm orifice	0.12-0.01
19-1	FT-200	200	0.051	1.85 mm orifice	0.01-0.12
20-1	FT-200	265	0.051	40 μm SMP	0.01-0.12

Table 4. Details of Operating Variables for Runs With Pure Liquids

Run number	Liquid medium	Column ID (m)	Distributor type	Operating range of superficial gas velocity (m/s)
W-1	distilled water	0.051	1.85 mm orifice	0.01-0.12
W-2	distilled water	0.051	1.85 mm orifice	0.12-0.01
W-3	distilled water	0.051	40 μm SMP	0.01-0.12
W-4	distilled water	0.229	19 × 1.85 mm PP	0.01-0.09
W-5	distilled water	0.229	5 × 1.00 mm PP	0.01-0.07
B-1	n-butanol	0.051	1.85 mm orifice	0.01-0.12
B-2	n-butanol	0.051	40 μm SMP	0.01-0.12

Table 5. Details of Operating Variables for Runs With Non-Wax Liquid Mediums

Run number	% by weight of n-butanol in aqueous soln.	% by weight of CMC in aqueous soln.	Column ID (m)	Distributor type	Operating range of superficial gas velocity (m/s)
B-3	1.0	0.0	0.051	1.85 mm orifice	0.01-0.12
B-4	1.0	0.0	0.051	1.85 mm orifice	0.12-0.01
B-5	1.0	0.0	0.051	40 μm SMP	0.01-0.12
B-6	1.0	0.0	0.051	1.00 mm orifice	0.01-0.12
B-7	0.5	0.0	0.051	1.85 mm orifice	0.01-0.12
B-8	0.5	0.0	0.051	40 μm SMP	0.01-0.12
B-9	1.0	0.1	0.051	40 μm SMP	0.01-0.12
B-10	1.0	0.1	0.051	1.85 mm orifice	0.01-0.12
B-11	1.0	0.1	0.051	1.85 mm orifice	0.12-0.01
B-12	1.0	0.1	0.051	1.00 mm orifice	0.01-0.12
B-13	1.0	0.5	0.051	1.85 mm orifice	0.01-0.12
B-14	1.0	0.5	0.051	40 μm SMP	0.01-0.12
B-15	1.0	0.5	0.051	1.00 mm orifice	0.01-0.12
B-16	1.0	0.0	0.229	19 × 1.85 mm PP	0.01-0.12
B-17	1.0	0.0	0.229	19 × 1.00 mm PP	0.01-0.12
B-18	1.0	0.1	0.229	19 × 1.00 mm PP	0.01-0.12
B-19	1.0	0.1	0.229	19 × 1.85 mm PP	0.01-0.12
B-20	1.0	0.5	0.229	19 × 1.85 mm PP	0.01-0.09
B-21	1.0	0.5	0.229	19 × 1.00 mm PP	0.01-0.09

Table 6. Physical Properties of Waxes.

Wax Type	Temp. (°C)	Density (kg/m^3)	Viscosity (mPa.s)	Surface Tension (N/m)	Reference
Krupp wax	200	723	3.0		Calderbank et al. (1963)
	230	705	2.2		
	260	694	1.6		
Paraffin wax	143	730	13.0	0.029	Deckwer et al. (1980)
	220	690	4.0	0.024	
	260	670	2.0	0.021	
FT-200 wax	149		4.4		Kuo et al. (1985)
	204		2.2		
	260	720	1.7	0.024	
FT-200 wax	150		4.4		This work
	200	712	2.8		
	230		2.4		
	265	675	1.9 *		
FT-300 wax	150		6.4		This work
	200	722	4.2		
	230	706	3.6		
	265	681	2.7 *		
SASOL's Arge wax	150		4.2		This work
	200	701	2.9		
	230		2.5		
	265	655	2.0 *		

* estimated from data at lower temperatures.

Table 6. Physical Properties of Waxes (contd.).

Wax Type	Temp. (°C)	Density (kg/m^3)	Viscosity (mPa.s)	Surface Tension (N/m)	Reference
MOBIL REACTOR WAXES					
Run CT-256-4	149		6.1		Kuo et al. (1985)
	204		4.3		
	260		3.4	0.026 - 0.027	
Run CT-256-5	149		17.6		Kuo et al. (1985)
	204		8.5		
	260		5.5	0.028	
Run CT-256-7	149		8.2		Kuo et al. (1985)
	204		4.1		
	260		2.3	0.026 - 0.027	
Run CT-256-8	149		13.1		Kuo et al. (1985)
	204		6.8		
	260		-	0.026 - 0.027	
Run CT-256-9	149		5.7 - 7.5		Kuo et al. (1985)
	204		3.1 - 4.0		
Run CT-256-11	149		6.1 - 6.7		Kuo et al. (1985)
	204		3.2 - 3.7		
Run CT-256-4	150		9.1		This work
CT-256-7	200		5.5		
composite	230		4.5		
	265		3.9 *		
Run CT-256-5	150		13.9		This work
CT-256-8	200		7.3		
composite	230		5.7		
	265		3.9 *		
Run CT-256-9,	150		6.5		This work
CT-256-11,	200	716	3.8		
CT-256-12	230		3.1		
composite	265	674	2.3 *		

* estimated from data at lower temperatures.

Density Measurements

Densities of various waxes were estimated by measuring the hydrostatic head for known heights of liquid in the 0.051 m ID glass column. The differential pressure cell (Validyne Model DP-15) was used to measure the hydrostatic head corresponding to a known liquid height. Hydrostatic heads were taken for various heights of liquid levels. This measurement was repeated two times. Before the measurements with wax, the pressure cell was calibrated using distilled water. The column was then preheated to the desired temperature and hot wax introduced into the column. The density of wax at the measured temperature was obtained from the slope of the hydrostatic head versus height plot, after appropriate corrections for the calibration factor. Results of these measurements are shown in Table 6 together with literature values (Calderbank *et al.*, 1963; Deckwer *et al.*, 1980; Kuo *et al.*, 1985). The measured values are in good agreement with the literature values. The effect of temperature on density was as expected, i.e. density decreases as temperature increases. These results also show that different types of waxes have similar densities between 655 and 694 kg/m^3 in the temperature range 260-265 °C.

Viscosity Measurements

Viscosity measurements were made in a Brookfield viscometer (LV series, 2.5X) using a cylindrical spindle (SC4-18) operating at 60 rpm. A Brookfield Thermosel system allowed measurements up to temperatures of 250 °C. The measurements were made in the temperature range 150-230 °C and the wax viscosity at higher temperatures was estimated from data at lower temperatures assuming Arrhenius type of dependence of viscosity on temperature. The system was first calibrated using standard silicone oils of known viscosities, 5.1 and 8.9 mPa.s at 25 °C, and distilled water, 0.89 mPa.s. Standard liquids were used before and after viscosity measurements with waxes to monitor device drift.

Results obtained from these measurements are presented in Table 6 along with data from literature. Comparison of data obtained with the same type of wax is possible only for FT-200 and some of Mobil's reactor waxes. Values of viscosity of FT-200 paraffin wax obtained in this study and Mobil's study (Kuo *et al.*, 1985) are in good agreement at low (~ 150 °C) and at high (~ 260 °C) temperatures, whereas the agreement is not so good at the intermediate temperatures (~ 200 °C). Viscosities of the composite Mobil reactor wax from runs 4 and 7 are consistently higher than values reported by Kuo *et al.* for either run 4 or run 7 waxes, whereas viscosities of the composite, from runs 5 and 8, are between values reported by Kuo *et al.* for waxes from the two runs. Viscosities of the composite from runs 9, 11 and 12 are in good agreement with values reported by Kuo *et al.* for waxes produced in runs 9 and 11. Kuo *et al.* reported values of viscosity of waxes samples produced at different times during the run.

Surface Tension

The surface tension of different waxes was not measured in the present study. However, from the data reported in the literature it may be concluded that different waxes have similar values of surface tension (e.g. results from Deckwer *et al.*, 1980; and Kuo *et al.*, 1985 are comparable)

The data summarized in Table 6 show that physical properties of different waxes at a given temperature are similar. In particular there are no significant differences in physical properties between the paraffin and the reactor waxes at higher temperatures (260-265 °C).

2. Aqueous Mixtures

Samples for physical property measurements were taken from fresh mixtures and spent mixtures. This was intended to monitor any degradations in physical properties of the mixture through a run. Samples of aqueous mixtures were categorized into the following groups:

1. Newtonian mixtures (distilled water and aqueous solutions of butanol).
2. Non-Newtonian mixtures (all aqueous mixtures containing CMC).

Density Measurement

Densities of aqueous mixtures were measured using a density meter, Mettler PAAR digital densitymeter DMA 35. The instrument measured the density and temperature of the mixture. The instrument was first calibrated using distilled water before samples of liquid mixtures were measured.

Results of these measurements together with literature values are presented in Tables 7–9. Density values for Newtonian liquids (see Table 7) are in good agreement with literature values, whereas, for non-Newtonian mixtures (Table 8) literature values are slightly higher than the measured values probably because literature values were obtained by dissolving CMC in tap water.

Surface Tension Measurement

Surface tensions of aqueous mixtures were measured using a Fisher Surface Tensiometer model 20. Details of the experimental procedure are described in APPENDIX E and the results of these measurements are presented in Tables 7–9. Measured values of surface tension for Newtonian liquids (aqueous solutions

Table 7. Physical Properties of Newtonian Liquid Mixtures at 24 °C

Liquid	Viscosity (mPa.s)	Surface Tension (N/m)	Density (kg/m^3)	Reference
Distilled water	0.9	0.071	996	Literature values
n-butanol	2.61	0.0241	808	Literature values
0.5% by weight of n-butanol in distilled water	0.9	0.051	996	This work
1.0% by weight of n-butanol in distilled water	0.91	0.042	995	This work
0.5% by weight of n-butanol in tap water	0.9	0.061	996	Fan *et al.* (1986)
1.0% by weight of n-butanol in tap water	0.92	0.054	995	Fan *et al.* (1986)

Table 8. Physical Properties of Fresh non-Newtonian Liquid Mixtures at 24 °C

Column ID (m)	% by weight of n-butanol in aqueous soln.	% by weight of CMC in aqueous soln.	Consistency index, K ($Pa.s^n$)	Flow behavior index, n (-)	Surface tension (N/m)	Density (kg/m^3)	Reference
0.051	1.0	0.1	0.047	0.745	0.044	995	This work
0.229	1.0	0.1	0.026	0.822	0.045	995	This work
0.051	1.0	0.5	0.713	0.577	0.048	997	This work
0.229	1.0	0.5	0.773	0.575	0.049	997	This work
0.154	0.0	0.1	0.05	0.76	N/A	N/A	Kelkar and Shah (1985)
0.1-1.0	0.0	0.1	0.012	0.80	0.073	1000	Haque *et al.* (1986)
0.1-1.0	0.0	0.5	0.061	0.70	0.072	1003	Haque *et al.* (1986)

Table 9. Physical Properties of Spent non-Newtonian Liquid Mixtures at 24 °C

Column ID (m)	% by weight of n-butanol in aqueous soln.	% by weight of CMC in aqueous soln.	Consistency index, K ($Pa.s^n$)	Flow behavior index, n (-)	Surface tension (N/m)	Density (kg/m^3)
0.051	1.0	0.1	0.027	0.828	0.044	995
0.229	1.0	0.1	0.012	0.929	0.053	996
0.051	1.0	0.5	0.546	0.608	0.049	997
0.229	1.0	0.5	0.578	0.594	0.053	998

of butanol) were lower than stated values from the literature, this may be due to different sampling and mixing techniques.

Viscosity Measurement

Viscosities of aqueous mixtures used in this study were measured using a concentric cylinder viscometer (Fann viscometer model 50C). For non-Newtonian mixtures, viscosities at different shear rates were measured as apparent viscosity (details of the experimental procedure are described in APPENDIX E) and results of these measurements are tabulated in Tables 7–9.

For Newtonian mixtures, the measured values (see Table 7) were in good agreement with the literature values, whereas, for non-Newtonian mixtures there was a large discrepancy. This deviation might be due different types of CMC used by different workers, there are three types of CMC: low viscosity, medium viscosity, and high viscosity. In this study, high viscosity CMC was employed and little information is known about the CMC used by other workers, this makes comparison with existing values difficult. However, a mixture containing 0.1 wt. % CMC used in this study gave values of K and n which were similar to those obtained by Kelkar and Shah (1985) (see Table 8).

D. Effects of Butanol and CMC on Physical Properties

Measurements of physical properties revealed that, apart from inhibiting coalescence in the bubble column, addition of n-butanol lowers the surface tension of water. Figure 4 shows the effect of butanol concentration on surface tension and viscosity. In this study 0.5 wt. % of butanol in distilled water lowered the surface tension of water from 0.071 N/m to 0.051 N/m and 1.0 wt. % of

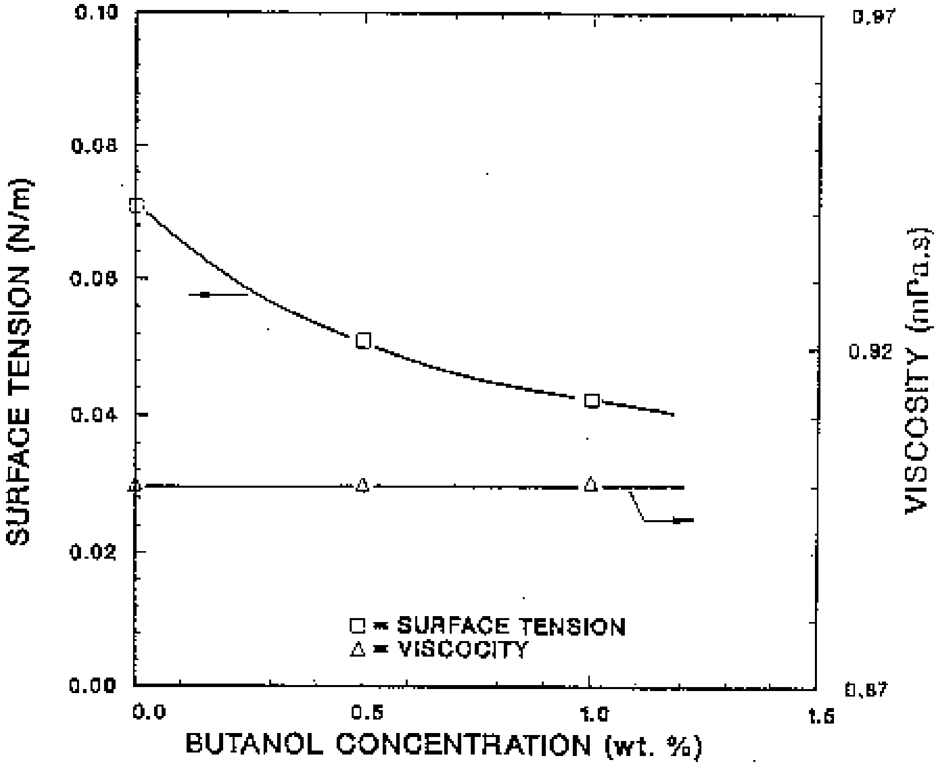
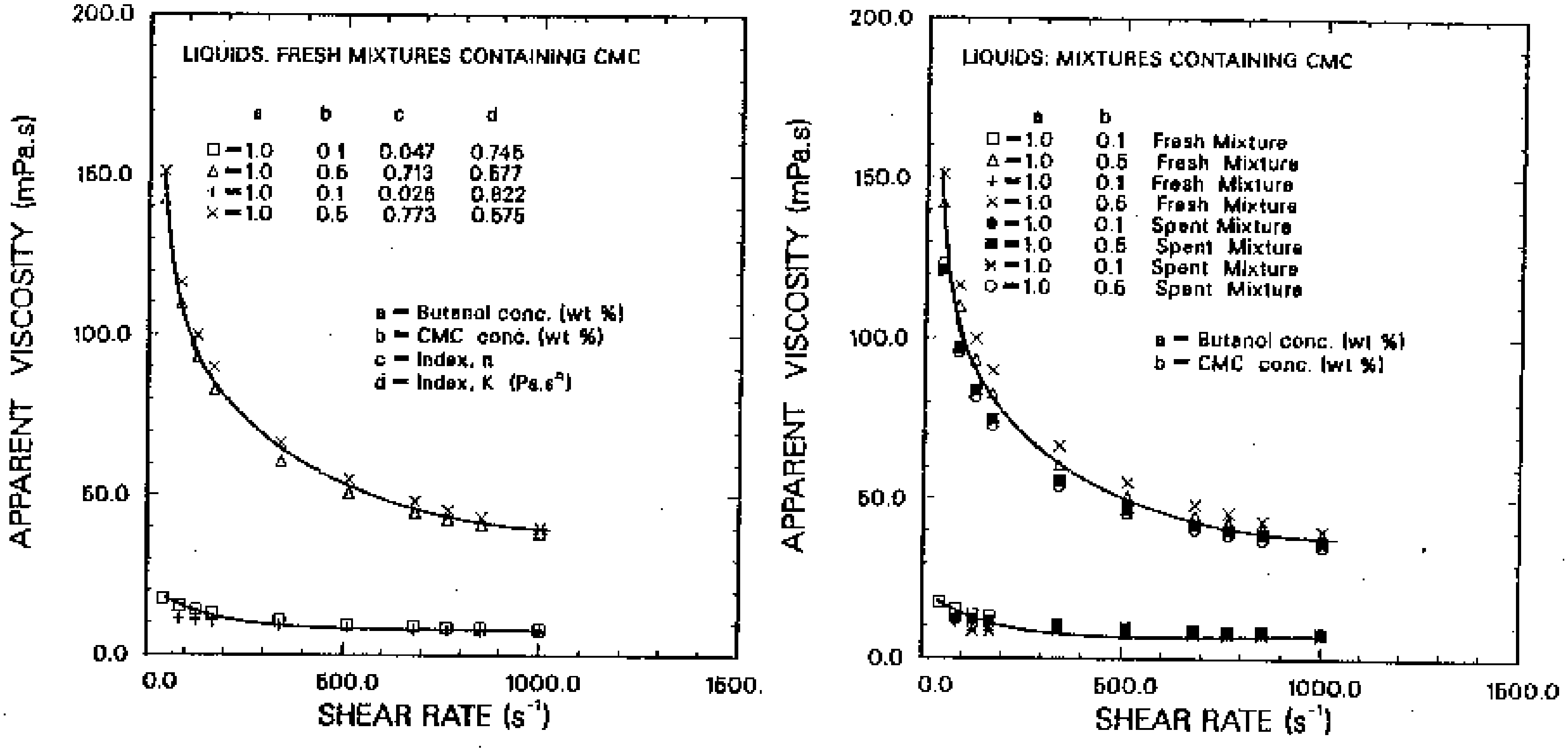


Figure 4. Effect of butanol concentration on surface tension and viscosity.

butanol lowered the surface tension to 0.042 N/m. However, no significant effects of alcohol concentration on viscosity and density were observed at these low alcohol concentrations.

An alcohol in distilled water acts like a surfactant. Alcohols consist of hydrophilic group (-OH) and a hydrophobic part (hydrocarbon structural group). These molecules are surface active, which means they will accumulate at the gas-liquid interface, e.g., in bubbly flow, on the liquid side of the interface the surface active molecules will tend to form a monolayer whose stability depends on the type, the concentration, and the size of surface active molecule (i.e., -OH, =CO, or -COOH). For primary alcohols, the stability of a monolayer increases with length of carbon chain. These organic molecules orient with their hydrophilic group into the liquid film surrounding the bubble and their hydrophobic part into the gas phase; hence, the liquid surface around the bubble becomes electrically charged. This surface polarization produces repulsive forces when two bubbles come close to each other. Thus the first step in bubble coalescence is prohibited. Increasing the concentration of butanol increases the concentration of the hydrophilic molecules on the surface resulting in a much lower surface tension. Opposite to this, CMC has a strong effect on the viscosity and only a minor effect on the surface tension and the density of the mixture. High concentrations of CMC may result in a very thick, jelly-like substance. Studies in bubble columns using aqueous solutions of CMC at concentrations (Buchholz *et al.* 1978; Franz *et al.* 1980; Nakanoh and Yoshida, 1980; Schumpe and Deckwer, 1982; Haque *et al.* 1986; and Vatai and Tekic, 1987.) have shown that the rate of coalescence is much higher for CMC solutions than for pure water. However, no studies have been reported where CMC was added to a non-coalescing system such as alcohol solutions.

Figure 5 (a) shows the apparent viscosities at different shear rates for different mixtures containing CMC. The CMC mixtures exhibit high apparent viscosities at low shear rates and a fairly constant value at high rates. The apparent viscosities increased with increasing concentration of CMC. However, slightly different values of the apparent viscosities were obtained for mixtures used in the large column and the small column, this might have been due to the effect of mixing procedure. It was much easier to dissolve small quantities of CMC for the small column than large amounts for the large column where vigorous mixing was required to dissolve the CMC. Several workers, e.g., Schürgel (1981) and Haque *et al.* 1986 have reported that viscosity of CMC solution is time dependent and since the solution decomposes with mixing. This property is illustrated in Figure 5 (b) where the apparent viscosities of fresh and spent mixtures are shown. The apparent viscosities of the spent mixtures were slightly lower than those of the fresh mixture.



a

b

Figure 5. Apparent viscosity versus shear rate for non-Newtonian mixtures.