

Figure 9. Solubility of CO<sub>2</sub> in MEA/MDEA aqueous solutions at 80 °C: points, experimental data; solid lines, smoothed values.

### Conclusion

The equilibrium solubility data of CO<sub>2</sub> into the blends of primary and tertiary amines, aqueous mixtures of MEA and MDEA, have been reported at temperatures of 40, 60, 80, and 100 °C and at CO<sub>2</sub> partial pressures from 1.0 to 2000 kPa. The mixtures of amines studied are 30 wt % MDEA, 12 wt % MEA +

18 wt % MDEA, 24 wt % MEA + 6 wt % MDEA, and 30 wt % MEA. Solubilities of CO<sub>2</sub> in 15.3 wt % MEA aqueous solution at 40 °C, previously reported by other investigators in the literature, have also been studied in this work to test the apparatus and to confirm the sampling and analytical procedures. The solubility data obtained in this work are generally in good agreement with the data reported by other investigators.

Registry No. MEA, 141-43-5; MDEA, 105-59-9; CO<sub>2</sub>, 124-38-9.

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## Solubility of Ethylene in Benzene at Pressures to 9 MPa and Temperatures from 353 to 433 K

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An experimental procedure for measuring the solubility of ethylene in benzene at elevated temperatures and pressures is described. The solubility has been measured as a function of pressure at six temperatures (353, 373, 393, 413, 423, and 433 K), and the results have been presented in tabular form and also in graphs. In addition an empirical equation has been developed which fits the measured data with an average error of 2.8%. Comparisons with the relevant literature data illustrate the significant differences which exist among the solubility data recorded by previous workers.

### Introduction

The studies described were prompted by commercial interest in optimizing the production process and product structures for some speciality products manufactured by copolymerizing ethylene with vinyl esters. In order to properly analyze kinetic data from polymerization experiments, values of the solubility of ethylene in benzene were required for a range of reactor operating conditions. A review of the relevant literature showed significant discrepancies among the reported solubility values. Consequently it was necessary to measure these values.

### Materials

The ethylene was purchased from Commonwealth Industrial Gases of Australia (a subsidiary of British Oxygen) as their

highest purity grade, which is better than 99.5 wt % pure. The benzene was purchased from B.D.H. Australia as their Univar grade, which was also rated as better than 99.5 wt % pure.

### Experimental Section

The general operating procedure is described first, and subsequently the details of the sampling and analyses for ethylene are presented.

The equipment diagram is shown as Figure 1. Experiments were carried out in a 1.0-L stainless steel reactor, fitted with a "Magnedrive" stirrer, which was set at 500 rpm for all runs. Temperature control was effected by means of an external heating element with a "Eurotherm" P.I.D. controller. Cold water was passed through an internal cooling coil to correct any overshoot of temperature which occurred. The temperature control was within  $\pm 1$  K. The maximum operating conditions of 9 MPa and 433 K were well below the rated maximum working conditions of the reactor, which were 34 MPa and 616 K. As an additional safety measure, the reactor was fitted with a rupture disk rated at 22 MPa at 295 K (the bursting pressure would be less than this at elevated temperatures). Whenever the reactor was dismantled and reassembled, the system was leak-tested with helium.

Each solubility measurement was initiated by first purging the reactor with ethylene. The reactor was then pressurized to approximately 5000 kPa with ethylene, and approximately 400 mL of benzene was pumped in. The Magnedrive stirrer was switched on and set to 500 rpm. The reactor was then brought

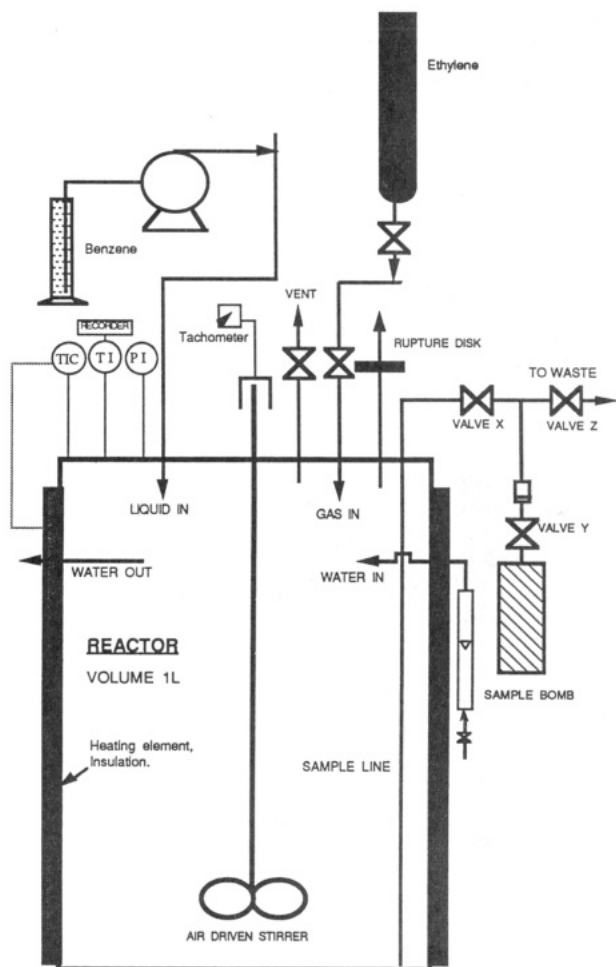


Figure 1. Equipment diagram.

up to the measurement temperature and the pressure vented slowly down to the desired pressure. Samples were taken in preweighed stainless steel sample bombs. The bombs were reweighed after sampling so that the total mass of the sample,  $M_t$ , could be calculated. Five samples were taken at each  $(T, P)$  condition. The reactor pressure was topped up with ethylene when necessary.

The solubility of ethylene in benzene was calculated by eqs 1 and 2 for each sample. The average value was calculated and taken to be the solubility for the measurement temperature and pressure. The standard deviation of the five values was calculated to give an indication of the precision of the method.

$$W_o = M_e / M_t \quad (1)$$

$$X_o = \frac{78.1}{78.1 + 28.1 \left( \frac{1}{W_o} - 1 \right)} \quad (2)$$

$M_e$  = mass of ethylene as calculated from eq 3

$M_t$  = total mass of the sample

$W_o$  = weight fraction of ethylene in the sample

$X_o$  = mole fraction of ethylene in the sample

An "on-line" sampling technique by which samples could be switched directly from the body of the liquid in the reactor to a gas chromatograph was explored and then discarded in favor of the technique using sample bombs. This manual-sampling technique although work-intensive had the advantage that it was reliably leak proof (unlike gas chromatograph sampling valves)

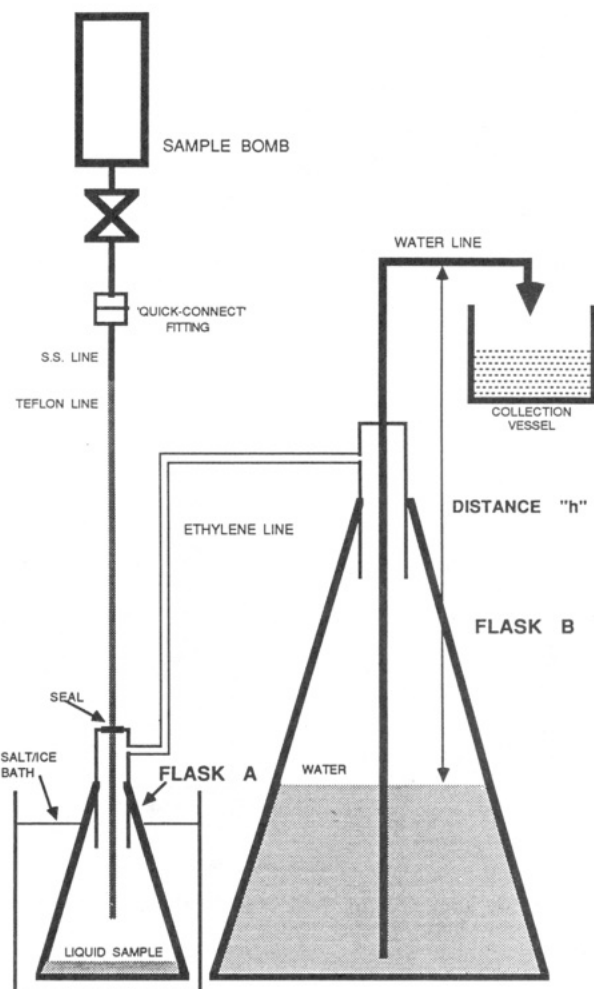


Figure 2. Ethylene quantitation and sample collection.

when utilized at elevated temperature and pressures.

The sample bombs were designed to be as light as possible, bearing in mind the safety requirements for high-temperature/high-pressure work. The magnitude of the sample bomb volume was chosen as a compromise between the desire for accurate analytical data and the desire to give minimal disturbance to the reaction system under study. A sample bomb volume of approximately 10 cm<sup>3</sup> was chosen, as this gave an insignificant pressure drop (approximately 50 kPa/sample or  $\approx 0.7\%$  of total reactor pressure), while giving a sample mass of 9–11 g. The mass of an empty sample bomb was approximately 440 g. This could be weighed accurately to  $\pm 5$  mg.

Each sample bomb was cooled and then connected to a Teflon line which passed into a small flask (labeled A, as shown in Figure 2). The sample bomb valve was slowly opened when releasing the sample. The "quick-fit" glass connection on the flask enabled the benzene to remain in the flask while the gaseous ethylene passed on via plastic tubing to flask "B". Flask A was held in a salt/ice bath at  $-15$  °C to reduce the vapor pressure of benzene to less than one-hundredth of an atmosphere. This ensured that the benzene content of the collected ethylene was negligible. The ethylene, upon entering flask B displaced water, which was collected and weighed. Because the ethylene was slowly released, it reached ambient temperature while passing to the collection vessel. This was checked periodically with a thermocouple. Thus with measurement of temperature,  $T_a$  (K), and pressure,  $P_a$  (Pa), and water density,  $\rho$  (g cm<sup>-3</sup>), and with a minor pressure correction for height "h" ( $h$  is defined in Figure 2, where it can be seen that the pressure of the collected ethylene would be affected by the magnitude of  $h$ ), the mass of ethylene present in the

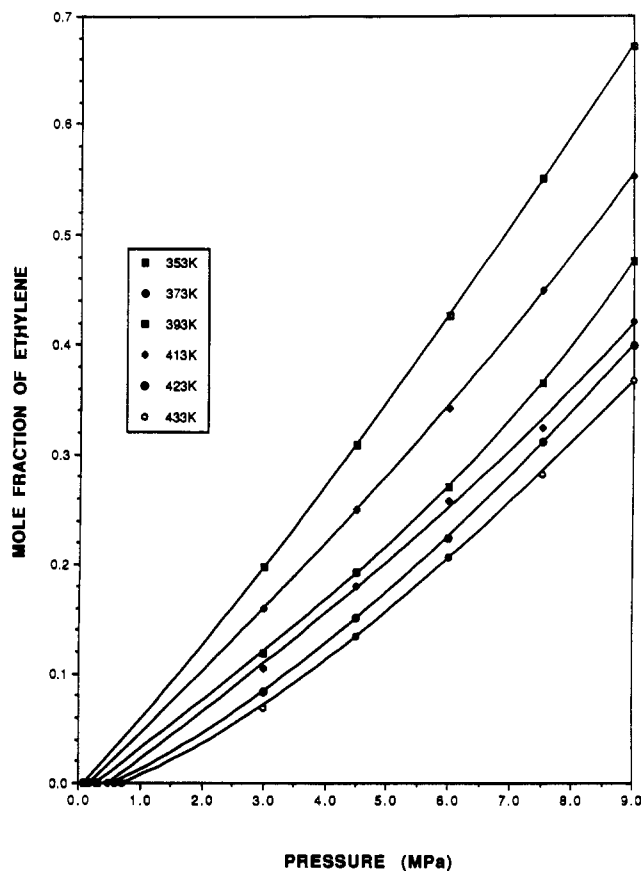


Figure 3. Solubility of ethylene in benzene at 30 combinations of temperature and pressure.

sample could be calculated (as one volume of gas would displace one volume of water). The compressibility factor for ethylene (the factor "z" as defined in the gas equation  $PV = znRT$ ) was taken as a constant (4),  $z = 0.994$ , at average room conditions of 288 K and 101.3 kPa. As the height  $h$  was directly related to the volume of water displaced, eq 3 was derived to directly calculate the mass of ethylene ( $M_e$ ) from the mass of displaced water ( $M_w$ ). The solubility of ethylene in water is so low that no correction was needed to allow for loss of ethylene to the water phase when water was displaced:

$$M_e = \frac{28.1M_w}{zRT_a\rho} \left[ P_a + 2.30\rho g \left( \frac{M_w}{\rho} \right)^{1/3} \right] \quad (3)$$

## Results

Five measurements of the mole fraction of ethylene in benzene were made at each of thirty temperature–pressure combinations. The mean value of the ethylene mole fraction for each temperature–pressure condition, together with the calculated standard deviation, is presented in Table I. The results are also presented in Figure 3 as plots of mole fraction of ethylene versus pressure for each of the six temperatures studied.

In order to make quantitative comparisons between the data obtained in these studies with that in the literature, mathematical relationships between the mole fraction of ethylene (i.e.  $X_e$ ) and the temperature and absolute pressure ( $P$  (MPa)) were developed. The expression shown below was found to give a very satisfactory fit to the data

$$X_e = a_1P + a_2P^2 + a_3\frac{P}{T} + a_4\frac{P^2}{T} + a_5 \quad (4)$$

where  $T$  = temperature ( $^{\circ}\text{C}$ ) and  $P$  = absolute pressure (MPa).

Table I. Solubility of Ethylene in Benzene

mole fraction of ethylene	standard deviation	pressure/MPa
Temperature = 353 K		
0.197	0.002	3.0
0.308	0.003	4.5
0.426	0.008	6.0
0.551	0.010	7.5
0.672	0.013	9.0
Temperature = 373 K		
0.159	0.006	3.0
0.250	0.004	4.5
0.342	0.007	6.0
0.449	0.009	7.5
0.554	0.006	9.0
Temperature = 393 K		
0.119	0.002	3.0
0.192	0.006	4.5
0.270	0.002	6.0
0.365	0.004	7.5
0.475	0.009	9.0
Temperature = 413 K		
0.104	0.003	3.0
0.180	0.003	4.5
0.257	0.004	6.0
0.324	0.005	7.5
0.421	0.009	9.0
Temperature = 423 K		
0.083	0.004	3.0
0.151	0.005	4.5
0.224	0.004	6.0
0.311	0.005	7.5
0.399	0.006	9.0
Temperature = 433 K		
0.069	0.004	3.0
0.134	0.005	4.5
0.207	0.010	6.0
0.282	0.008	7.5
0.367	0.014	9.0

This equation has no theoretical basis—it was developed solely as a convenient means by which the various data may be compared. In some cases vapor–liquid equilibria may be estimated from equations of state (Reid et al., 1977). However these procedures are complicated when one or more components are close to their respective critical points (as is the case for ethylene in this study).

Accordingly the data obtained in this study, together with literature data which fell within the same range of operating conditions, were fitted to eq 4 by regression analysis using an IMSL computer subroutine, `RLSEP` (International Mathematical and Statistical Libraries, Inc., Houston, TX). The results of the regression are given in Table II. Where appropriate, points were included in the above regressions which indicate the liquid mole fraction of ethylene is zero at the boiling point of benzene. Plots were constructed at  $T = 353, 393,$  and  $423$  K involving data obtained in the present work, as well as data obtained by other workers. These plots are shown as Figure 4a–c. It may be noted that a plot at 433 K was not constructed because only one literature reference (3) contained data for this temperature.

## Discussion

It can be seen from Figure 3 that the solubilities of ethylene in benzene measured in this work form smooth lines when plotted against pressure at constant temperature. This, together with the low values of standard deviation ( $\sigma$ ), suggests an accurate experimental technique. From the values of  $\sigma$  listed in Table I, the average error of the solubility can be given as  $\pm 2.8\%$ . As expected from a hydrocarbon binary system of this kind, the solubility was found to increase with increasing

Table II. Regression of Solubility Data for Equation 4

	this work	Zhuze and Zurba (6)	Lyubetskii (3)	Hiraoka (2)	Ellis (1)
regression coefficients:					
$a_1 \times 10^2$	-1.877	0.948	0.535	1.423	5.996
$a_2 \times 10^3$	3.187	0.002	1.033	0.257	1.759
$a_3$	6.967	2.892	5.107	5.664	0.0
$a_4 \times 10$	-1.846	2.409	0.535	-0.656	0.0
$a_5 \times 10^2$	-1.292	-0.863	-1.764	-2.143	0.141
no. of data points	36	21	27	8	10
temperature range/K	353-433	348-423	338-435	373-423	348
pressure range/MPa	3.0-9.0	3.2-12.0	3.0-9.1	4.1-10.1	1.5-9.1
relative standard deviation <sup>a</sup>	2.8	3.6	5.3	2.8	3.1

<sup>a</sup> Expressed as a percentage of the mean.

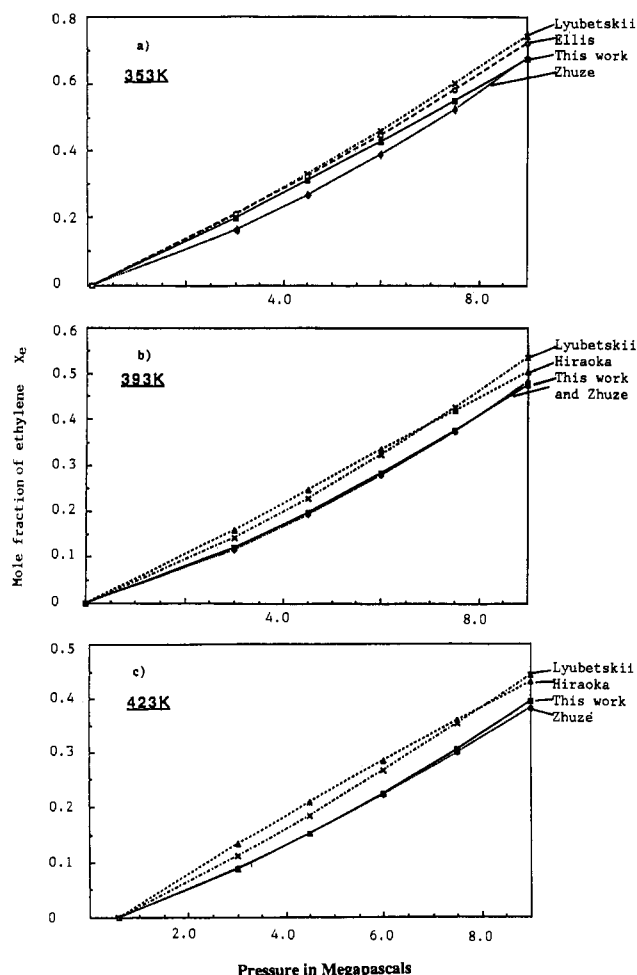


Figure 4. Comparison of ethylene solubilities in benzene determined by several workers, including this work: ■, this work; ◆, Zhuze and Zurba (6); ×, Lyubetskii (3); ○, Ellis et al. (1); △, Hiraoka (2).

pressure and decreasing temperature. The comparison of the results of this work with the literature values is illustrated in Figure 4. Figure 4 also illustrates the discrepancies in the values available in the literature. The values of solubility given by Hiraoka (2) and Lyubetskii (3) were consistently higher than the values of Zhuze and Zurba (6) and the present work. This is most probably due to the large differences between the respective techniques used. Lyubetskii used a method whereby mixtures of ethylene and benzene of known composition were prepared, and the bubble and dew points of the mixtures were then measured at several pressures inside a pressurized tube. This was achieved by judging when the first bubble of vapor (or drops of liquid) appeared by looking through a window in the side of the tube. It would seem that this method would be fairly subjective. Hiraoka achieved equilibrium by bubbling ethylene through the liquid benzene. It is not stated how much time was

allowed for equilibrium conditions to be established; consequently these results are open to question.

An experimental setup such as the one used in the present work, whereby the ethylene/benzene mixture could be violently agitated, would have ensured equilibrium conditions were reliably and quickly established. The analytical technique used by Hiraoka was not described. Thus, discussion of this aspect is not possible. While the values of Zhuze and Zurba agree more closely with those of the present work, little information is given as to the method used by these workers in determining the solubility. A method similar to that used by Lyubetskii appears to have been employed.

It appears that the  $T, P$  dependence of the solubility can be adequately described by an empirical relation such as eq 4. Common expressions used to fit data for the solubility of ethylene in organic liquids are often of the form given in eq 5

$$\ln X_e = a_1 \ln P + \frac{a_2}{T} + a_3 \quad (5)$$

(4), although values of temperatures and pressures have generally been lower than those for the present study. When the data of the present work was fitted to eq 5, an average error of 5.8% resulted. This compares with an error of 2.8% when the data was fitted to eq 4, which also gave a much better fit to the data from all other sources. As the principal criterion was accurate fitting of the data (for comparison of these and literature data), eq 4 was given preference over eq 5.

## Conclusions

A method of measuring the solubility of ethylene in benzene has been described. This method is suitable for conditions of high temperature and pressure and gives very good reproducibility.

An empirical expression (eq 4) has been developed for the ethylene/benzene system, involving the solubility of ethylene as a function of temperature and pressure. This equation fits the data well, with an average error of 2.8%.

The corresponding solubility data found in the literature contained substantial discrepancies. These may have arisen from differences in the experimental techniques adopted by the various workers. The data measured in the present work was generally closest to that of Zhuze and Zurba (6), although this was not true for most of the measurements made at 353 K.

## Nomenclature

$g$	gravitational acceleration, $9.8 \text{ m s}^{-2}$
$M_e$	mass of ethylene as calculated from eq 3
$M_t$	total mass of sample collected in the sample bomb
$M_w$	mass of water displaced when the ethylene gas was collected
$P, P_a$	pressure, Pa, kPa, or MPa
$R$	gas constant
$T, T_a$	temperature, K or °C
$V$	volume

$W_e$  weight fraction of ethylene in the liquid sample  
 $X_e$  mole fraction of ethylene in the liquid sample  
 $Z$  compressibility factor  
 $\rho$  water density, g cm<sup>-3</sup>

Registry No. Ethylene, 74-85-1; benzene, 71-43-2.

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## Quaternary Liquid-Liquid Equilibrium Studies on Hydrocarbon-Solvent Systems

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Quaternary equilibrium tie-line data have been determined at 60 °C for the model hydrocarbon mixtures of naphtha and kerosene with sulfolane and triethylene glycol solvents. The study was carried out in order to understand the mechanism of simultaneous extraction of aromatics from naphtha and kerosene feedstocks. Benzene-heptane and 1-methylnaphthalene-dodecane model mixtures were chosen as feeds representing naphtha and kerosene cuts, respectively. The liquid-liquid equilibrium data so obtained have been predicted by the UNIFAC group contribution model. Group interaction parameters for groups which best represent triethylene glycol molecule were also calculated from the data available with the authors for those not available in the literature.

#### Introduction

Straight-run naphtha fractions when required for naphtha crackers and fertilizer units and kerosene fractions when required for use as aviation turbine fuel (ATF) and superior kerosene (SK) should not contain more aromatics than stipulated for these applications. These streams, therefore, require dearomatization to the extent that they become suitable for such applications. Dearomatization of naphtha (1) is done by conventional solvent extraction methods, whereas dearomatization of kerosene is done either by hydrogenation or by solvent extraction of aromatics. The present solvent extraction route for kerosene feedstocks is not attractive as this uses the cumbersome and obsolete technology of liquid sulfur dioxide extraction (2). The hydrogenation route for kerosenes, on the other hand, is attractive but is capital intensive.

An attractive scheme of simultaneous extraction (simex) of aromatics from naphtha and kerosene was tried earlier (3, 4). In this scheme, extract phases from the naphtha and kerosene columns are solvents for each other. In the process, displacement of aromatics from the hydrocarbon phase to the solvent phase and vice versa results in dearomatization of these streams.

However, the simex mechanism is complex since it involves multicomponent systems. In the present study, liquid-liquid

equilibrium (LLE) data on model hydrocarbon mixtures representing naphtha and kerosene as feeds and their respective extract phases as solvents have been generated to understand the displacement mechanism. These LLE data have been correlated by the UNIFAC (5) solution model and will be useful in the simulation of the simex scheme. Solvents used in the present study were sulfolane, triethylene glycol (TEG), and sulfolane containing 3 wt % water.

#### Experimental Section

**Feeds Used.** Benzene and heptane were supplied by S-D Fine Chemicals PVT, Ltd., 1-methyl naphthalene (1-MN) was supplied by Koch Light Laboratory, Ltd., and dodecane was supplied by J. T. Baker Chemical Co., Phillipsburg, NJ. The purities were checked by gas chromatography (GC), which indicated that all hydrocarbons had a minimum purity of 99%.

**Determination of LLE.** The benzene-heptane model mixture, representing the naphtha feed, was mixed with solvent containing 10 wt % 1-MN, representing the kerosene extract phase and, thus, forming a quaternary system. Similarly, the 1-MN-dodecane model mixture, representing the kerosene feed, and solvent containing 10 wt % benzene, representing the naphtha extract phase, formed the second set of the quaternary system. The concentration of 1-MN or benzene in the solvent was arbitrarily fixed at 10 wt % on the basis of previous experience with the continuous extraction runs. Thus, the former system represented the naphtha column of a simex unit, and the latter represented the kerosene column. Batch LLE data were determined at 60 °C in a jacketed mixer-settler of 200-mL capacity with a thermometer pocket and a syringe stirrer. Temperature was maintained within  $\pm 0.05$  °C of the experimental temperature by using a thermostatic bath.

The known weights of the feed and solvent of known composition were taken in the mixer-settler and stirred well for 25 min to establish equilibrium between the phases. The phases were allowed to settle for about the same time at the same temperature and then withdrawn separately, weighed, and analyzed. Solvent was removed from the raffinate phase by a water washing and from the extract phase by azeotropic distillation with water (6).

The aromatics in the solvent-free extract and raffinate were determined by gas chromatography.

The benzene content in the system benzene-heptane-(solvent + 1-MN) and the 1-MN content in the system 1-MN-do-

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