Purification of Isoprene by Extractive Distillation with Dimethylformamide

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THE EFFECTIVENESS of dimethylformamide as an extractive distillation agent purifying isoprene was studied. It was selected from a group of recently evaluated solvents (*9*) on the basis of its good selectivity for the pentane-1-pentene separation, and because it has a low molecular weight, good thermal stability, ready availability, and negligible tendency to promote corrosion. Isoprene and 2-methyl-2-butene were used as the test system to evaluate the dimethylformamide.

Numerous other solvents have also been suggested for use in purification of isoprene and other diolefins, including acetone, 2-butanone (methyl ethyl ketone), pyridine, acetonitrile, propionitrile, acetic anhydride, amines, and furfural, both as pure components or in mixtures with water (*1, 4, 7, 8, 15-18*).

Also, the pilot column method for obtaining results was evaluated. In this method, a small sieve-tray column is operated at steady-state conditions, and various tray liquid samples are withdrawn and analyzed. From this information, relative volatilities are obtained by operating the column in a pinch region where results are independent of tray efficiency, or by operating away from the pinch region where tray efficiency must be known for the calculation of relative volatility from tray compositions.

The pilot column method for determining vapor-liquid behavior has two advantages over a conventional equilibrium still. In the latter, vapor and liquid composition often are very similar in value, requiring extreme care in sampling and analysis; in the pilot column, samples may be taken a number of trays apart and thus have larger composition differences. Also, many additional data useful later for design purposes are obtained along with the vapor-liquid behavior.

EXPERIMENTAL

A 1.5-inch diameter glass Oldershaw column containing 15 sieve trays was used. Each tray contained 237 holes each 0.055 inch in diameter; the hole spacing was also 0.055 inch. The outlet weir height was ¼ inch and the tray spacing was 2 inches. The column had specially designed thermowells and sample taps on every third tray.

Tray Efficiency of Oldershaw Column. Prior to the extractive distillation tests, tray efficiencies for the Oldershaw column were determined over a range of column flow rates using *n*-pentane-isopentane mixtures. These runs were made at total reflux and with a single still pot composition. Samples of the tray liquid were taken at steady state from the 2nd and 14th trays from the bottom; in nearly all runs the tray 14 liquid contained 70 to 74 mole % of isopentane.

The Fenske-Underwood total reflux equation was used to calculate the number of theoretical plates from the measured composition change and relative volatility (*19*). The relative volatility was computed from vapor pressure data (*2*) assuming ideal behavior in the gas and liquid phases. The liquid samples were analyzed by mass spectrometer. Tray efficiency was then calculated by dividing the number of theoretical plates by the actual number. The over-all column efficiency thus obtained was taken to be equal to the Murphree efficiency, E_{MV}, because the equilibrium and operating lines were essentially parallel. The Murphree efficiency was also taken to equal the point efficiency, E_{OG}, as the trays are small and the liquid on each tray is completely mixed.

The resulting efficiencies are plotted *vs.* F factor based on the total column cross section (Figure 1). Between $F = 0.1$ and $F = 0.54$, the efficiency decreases slightly from 55 to 51%.

Extractive Runs. In the extractive distillation runs, solvent-rich liquid from the still pot was recycled to tray 14 to maintain the desired solvent concentration on the trays. This recycle liquid was cooled, pumped through a rotameter to measure flow rate, and sent through a preheater before being discharged onto tray 14. A flow sheet of the equipment is shown in Figure 2. In all runs, the overhead vapors were totally condensed and returned to the top tray as reflux. Operating data, including the various temperatures, still pot to atmosphere pressure differential, and rotameter readings, were recorded after the establishment of steady-state conditions.

Samples of 2 to 4 ml. each were then withdrawn from trays 2 and 11 (from the bottom), and from the recycle liquid line. The liquid holdups on the trays were also measured. Liquids from the trays and the recycle line were analyzed by a Consolidated 21-103 mass spectrometer at atmospheric pressure, at F factors ranging from 0.09 to 0.37, at solvent concentrations in the liquid from 54 to 93 mole %, and at olefin concentrations in the liquid of from 42 to 72 mole % on a solvent-free basis. The resulting temperature range was from 117° to 201° F. Molar liquid to vapor flow rate ratios (L/V values) varied from 1.06 to 2.14 on a solvent-free basis. About half of the runs were made at the higher values of L/V which caused the tray composition to "pinch"; under these conditions, the relative volatility calculation was not appreciably affected by the value used for the tray efficiency.

CALCULATION PROCEDURE

Relative volatility values were obtained graphically from a modified McCabe-Thiele diagram. When compositions are expressed on a solvent-free basis, such a diagram is exact when solvent concentrations and gas and liquid flow rates are constant over the section of the tower considered (*14*). In present experiments, both solvent concentrations and flow rates were essentially constant between trays 2 and 11 over which the relative volatility values were determined.

Operating line points were located for trays 2 and 11; liquid compositions were determined by sampling, and vapor compositions were computed by over-all and component material balances with the recycle stream. Next, a relative volatility value was assumed, and a tray efficiency computed by the A.I.Ch.E. tray efficiency prediction method (*10*). Experimental *n*-pentane-isopentane efficiencies were used as a basis for these calculations. The number of actual steps each with an efficiency equal to the computed value lying between the terminal points on the

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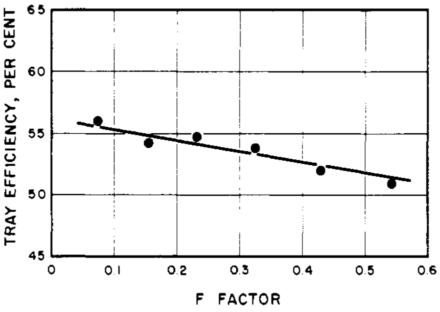
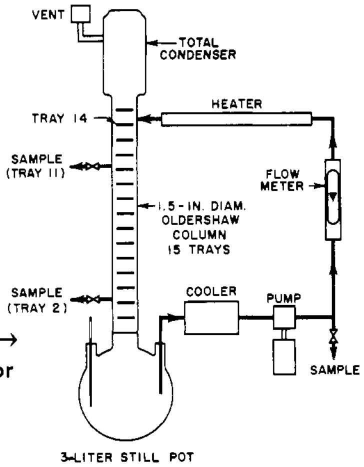


← Figure 1. Point efficiencies for pentane-isopentane system in Oldershaw column as function of throughput



→ Figure 2. Flow sheet for extractive runs

operating line was then determined. If this number was 9, the actual number of trays between the end points of the operating line, the assumed relative volatility was correct; if not, a new relative volatility was assumed and the procedure repeated until a match in the number of trays was obtained. The same procedure was used for the runs where pinch conditions existed on the solvent-free McCabe-Thiele diagram. In these instances, the computed relative volatility was not appreciably affected by the value used for the tray efficiency.

Calculation of Operating Line Points. The liquid analyses fixed the liquid compositions on trays 2 and 11, but the vapor compositions to these trays had to be computed by the following material balance equations:

$$V + R = L \tag{1}$$

$$y_S V + z_S R = x_S L \tag{2}$$

$$yV + zR = xL \tag{3}$$

In the above equations, V and L are vapor and liquid rates below any tray and R is the recycle rate, moles per second, respectively, y_S, z_S, and x_S are the solvent compositions in the vapor, recycle, and liquid, respectively, and y, z, and x are the olefin concentrations in the vapor, recycle, and liquid, respectively. All compositions are expressed in units of mole fraction. As measured values were available for R, z_S, z, x_S and x, and y_S was small and could be estimated, Equations 1 to 3 could be used to solve for the three unknowns, V, L, and y. These equations were applied first to tray 2 and then to tray 11. In all runs, the flow rates at these two trays differed by less than 4%, so that use of a straight operating line between these two points was justified.

Correlation of Pentane–Isopentane Efficiencies. To use the A.I.Ch.E. tray efficiency prediction method for the extractive system, values are required for the gas-phase and the liquid-phase efficiency of the particular tray design employed. Correlations for these efficiencies in terms of N_G and N_L are presented in the A.I.Ch.E. report for ordinary sieve trays (*11*), but they do not apply to trays containing holes of very small diameter. It was therefore necessary to determine efficiencies for the Oldershaw column experimentally.

The measured *n*-pentane–isopentane efficiencies are essentially point efficiencies, but they include both gas-and liquid-phase mass transfer resistances. The relationship between the point efficiency, E_{OG}, the gas-phase mass transfer resistance, $1/N_G$, and the liquid-phase mass transfer resistance, $(mV/L)/N_L$, is given by (*11*):

$$\frac{1}{-2.3 \log (1 - E_{OG})} = \frac{1}{N_{OG}} = \frac{1}{N_G} + \frac{mV/L}{N_L} \tag{4}$$

Absolute values of these resistances were calculated from the experimental values of E_{OG} by assuming that the ratio of gas-to liquid-phase mass transfer resistance for the Oldershaw trays at any given F factor is the same as the corresponding ratio for ordinary sieve trays. This approach is justifiable because the increased interfacial area produced by the tiny holes of the Oldershaw trays causes both N_G and N_L to increase by the same percentage.

The gas-phase mass transfer resistance for ordinary sieve trays was obtained from the data of Figure 3. These data (*12*) are for a tray containing $\frac{1}{8}$-inch diameter holes and were obtained for the ammonia-air system. Values of N_G for the ammonia-air-water system were multiplied by 0.85 to convert them to the pentane-isopentane system; this factor is the ratio of the Schmidt groups to the 0.5 power. Use of the 0.5 power for the Schmidt group correction is justifiably based upon experiments made at variable pressure in the A.I.Ch.E. program (*10*) and upon comparison of predicted and experimental efficiencies of industrial columns (*10*).

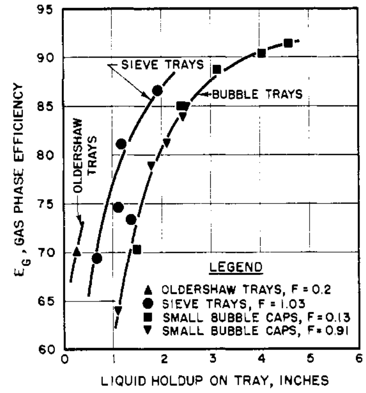


Figure 3. Gas-phase efficiencies for ammonia-air-water system as function of liquid holdup on tray

Sieve tray and bubble tray results from (*12*)

Oldershaw column result from this study

The liquid-phase resistance was estimated from the following correlation for sieve trays containing $\frac{3}{16}$-inch holes (*13*):

$$N_L = (100\, D_L^{0.5})\,(0.49F + 0.17)\,(t_L) \tag{5}$$

The average value of mV/L, the ratio of slopes of equilibrium curve and operating line, was taken as unity.

The resulting gas to liquid resistance ratios for ordinary sieve trays are plotted in Figure 4. The reason for the variation of these ratios with F factor becomes apparent when values of t_L, the average liquid contact time on each tray, are examined (Figure 4). Because all runs were carried out at total reflux, the t_L values increase as the gas throughput is reduced. And, because N_L is seen in Equation 5 to be controlled mainly by t_L, and because N_G is insensitive to both gas and liquid rate, the ratio of gas- to liquid-phase mass transfer resistance increases with decreasing gas throughput.

The computed results from Figure 4 were used with Equation 4 to solve for values of N_G and N_L from the experimental values of E_{OG} for the pentane-isopentane system. Results are shown in Figure 5. These values of N_G and N_L are from 11 to 30% higher than the corresponding values for ordinary sieve trays; in terms of efficiency, values of E_{OG} for the Oldershaw column are from 6 to 9 efficiency % higher than those for ordinary sieve trays for the pentane-isopentane system. A comparison of the Oldershaw column performance with that for ordinary sieve trays when the results are converted to the ammonia-air basis is given (Figure 3).

Calculation of Extractive Efficiencies. Equation 4 may be used to compute values of E_{OG} for the Oldershaw column when operating with the extractive system. Values of N_G at a given F factor (Figure 5) are corrected from the pentane-isopentane system over to the extractive system by multiplying by the ratio of the Schmidt numbers to the 0.5 power; this correction changes the N_G values by only 3% as the extractive system gas-phase properties are so similar to those for pentane-isopentane. Values of N_L at a given F factor (Figure 5) are corrected to the extractive system by multiplying by the D_L ratio to the 0.5 power and by the t_L ratio. The former multiplying factor averaged 0.78, while the latter varied from 1 to 0.1. Contact times in the extractive runs were low in some cases because of the high liquid rates resulting from the use of high solvent concentrations. The computed extractive efficiencies varied from 54 to 38%, and the ratios of gas- to liquid-phase mass transfer resistance varied from 0.93 to 2.75. The lower efficiency values were caused mainly by the lower liquid contact times.

Prediction of the D_L values for the extractive system which were required in the above calculations presented some difficulty. As the C_5 olefin and diolefin have similar physical properties, these two substances were treated as a single component having properties equal to the average of both. Values of $(D_L\mu_L)/T$ were then predicted at infinite dilution of the C_5 component in the solvent, and at infinite dilution of the solvent in the C_5. Values of D_L were predicted by the method of Chang and Wilke (5) using an association factor of 1.4 for the solvent. Liquid viscosities (μ_L) were estimated by Swanson (21) from his experimental data for various isoprene-2-methyl-2-butene-dimethylformamide mixtures at 77° F. and from viscosity-temperature data for dimethylformamide (6). A value of $(D_L\mu_L)/T$ for the tray liquid was obtained by linear interpolation between the infinite dilution values with respect to solvent composition. This procedure appears to be more valid according to the recent data of Anderson, Hall, and Babb (3) than the use of the Wilke recommendation (23).

Original data and computed results for all of the extractive runs are given in Table I; additional details are contained in the thesis of Swanson (21).

CORRELATION OF RESULTS

Results were correlated and extended by the ternary Margules equation as written by Wohl (24):

$$\log \gamma_M/\gamma_I = x_I^2 A_{MI} - x_M^2 A_{IM} + 2x_M x_I (A_{IM} - A_{MI})$$
$$+ x_S \Big\{ 2x_M A_{SM} - 2x_I A_{SI} + x_S (A_{MS} - A_{IS})$$
$$+ (x_I - x_M)\Big[\tfrac{1}{2}(A_{MI} + A_{IM} + A_{MS} - A_{SM} + A_{SI} + A_{IS}) \Big] - C^* \Big\} \qquad (6)$$

Subscript M is for 2-methyl-2-butene, I for isoprene, and S for the solvent, dimethylformamide.

The equation was simplified with the following assumptions:

1. 2-Methyl-2-butene-isoprene binary is ideal and $A_{MI} = A_{IM}$.
2. Hydrocarbon-solvent binary systems have symmetrical activity coefficient relationships—i.e., $A_{MS} = A_{SM}$ and $A_{IS} = A_{SI}$. This is nearly so in similar systems such as furfural-butene and furfural-butadiene (22).
3. Ternary effect was absent—i.e., $C^* = 0$ (20).
4. $x_I = x_M$. This is the average condition in the present runs, although composition of the liquid on the trays varied from 20 to 82 mole % 2-methyl-2-butene (solvent-free).

Under the above conditions, Equation 6 reduces to:

$$\log \gamma_M/\gamma_I = (A_{MS} - A_{IS})\, x_S \qquad (7)$$

To test the applicability of this simplified form of Wohl's equation, the experimental relative volatility values were converted to activity coefficient ratios by the relation $\gamma_M/\gamma_I = \alpha/(P_M/P_I)$. Vapor pressure values were obtained by extending the data of (2). Values of $(A_{MS} - A_{IS})$ were then computed as $(\log \gamma_M/\gamma_I)/x_S$ and are shown plotted as a function of temperature (Figure 6).

If the assumptions for the simplification of Equation 6 are correct, and if the predicted tray efficiencies are correct, a single correlation line should result. Inspection of Figure 6 shows this to be very nearly so; the experimental

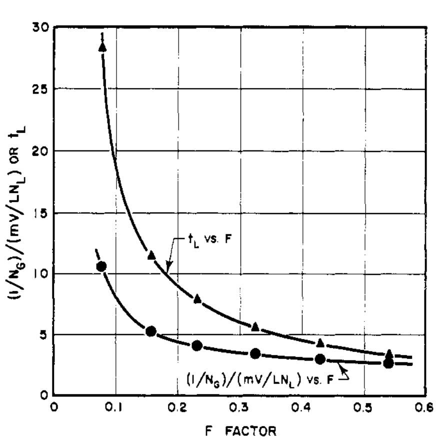


Figure 4. Predicted ratios of gas- to liquid-phase mass transfer resistance $(1/N_G)/(mV/LN_L)$, for pentane-isopentane system in Oldershaw column

Also shown are values of t_L, average liquid ccontact time on each tray in seconds

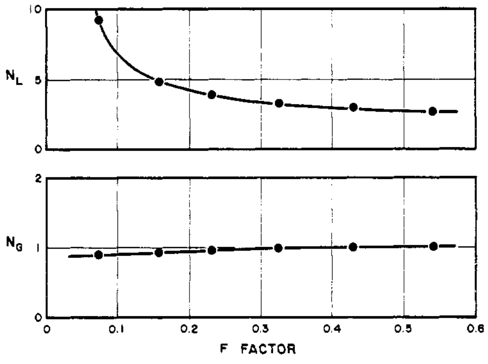


Figure 5. Values of N_G and N_L for pentane-isopentane system in Oldershaw column

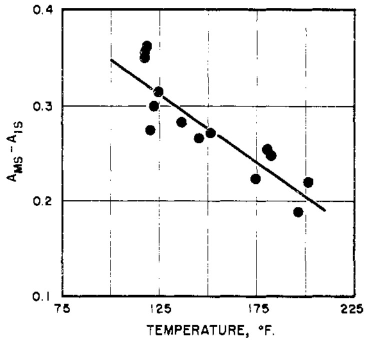


Figure 6. Experimental values of difference in Margules binary constants for olefin-solvent and isoprene-solvent systems as a function of temperature

Table I. Data and Results for Extractive Runs

Run Number	17	18	19	20	21	22	23
Flow rates, lb. moles/sec. × 10^3							
Recycle stream	15.4	21.3	32.3	61.6	15.4	21.3	36.7
Liquid on trays 2-11	27.2	29.8	38.7	65.3	24.0	25.9	40.2
Vapor to trays 2-11	11.9	8.47	6.36	3.65	8.63	4.68	3.42
Liquid on trays 2-11, SFB[a]	12.4	9.18	7.39	5.61	9.11	5.24	4.34
Vapor to trays 2-11, SFB[a]	11.7	8.26	6.07	3.25	8.45	4.56	2.80
F factor	0.37	0.27	0.21	0.13	0.27	0.15	0.10
t_L, sec.	4.0	3.8	3.0	1.8	4.6	4.0	2.9
Compositions, mole fraction olefin, SFB[a]							
Liquid on tray 2	0.412	0.384	0.380	0.395	0.570	0.568	0.586
Vapor to tray 2	0.421	0.393	0.398	0.445	0.582	0.589	0.627
Liquid on tray 11	0.668	0.657	0.582	0.437	0.800	0.745	0.638
Vapor to tray 11	0.689	0.688	0.632	0.531	0.826	0.787	0.707
Average conditions, trays 2–11							
Solvent compn. in liq., mole fraction	0.544	0.692	0.809	0.914	0.621	0.798	0.892
Temp., ° F.	117	124	145	184	118	136	174
Olefin compn. in liq., mole fraction SFB[a]	0.54	0.52	0.48	0.42	0.69	0.66	0.61
Tray efficiency							
N_G	1.09	1.07	1.04	0.98	1.06	0.98	0.95
$(1/N_G)/(mV/LN_L)$	2.17	1.79	1.37	0.93	2.43	1.63	1.68
E_{OG}	0.53	0.50	0.45	0.38	0.53	0.46	0.45
L/V, SFB[a]	1.06	1.11	1.22	1.73	1.08	1.15	1.55
$A_{MS} - A_{IS}$	0.355	0.315	0.266	0.247	0.362	0.283	0.223
α_{MI}, trays 2–11	1.35	1.43	1.46	1.49	1.46	1.47	1.40
α_{MI}, without solvent	0.865	0.868	0.876	0.888	0.866	0.873	0.885
	24	25	26	27	28	33	34
Flow rates, lb. moles/sec. × 10^3							
Recycle stream	66.0	18.4	28.4	41.9	64.7	24.0	24.0
Liquid on trays 2–11	68.7	27.9	32.5	44.8	67.4	32.0	32.4
Vapor to trays 2–11	2.70	9.53	4.11	2.94	2.68	8.03	8.35
Liquid on trays 2–11, SFB[a]	4.94	10.1	5.14	4.21	4.72	10.7	11.5
Vapor to trays 2–11, SFB[a]	2.31	9.33	3.90	2.63	2.24	7.83	8.14
F factor	0.09	0.30	0.13	0.10	0.09	0.25	0.26
t_L, sec.	1.7	4.4	4.0	2.6	1.9	4.4	4.4
Compositions, mole fraction olefin, SFB[a]							
Liquid on tray 2	0.555	0.594	0.617	0.598	0.583	0.291	0.554
Vapor to tray 2	0.612	0.604	0.647	0.644	0.648	0.319	0.589
Liquid on tray 11	0.570	0.823	0.732	0.648	0.597	0.384	0.604
Vapor to tray 11	0.635	0.846	0.791	0.731	0.678	0.446	0.660
Average conditions, trays 2–11							
Solvent compn. in liq., mole fraction	0.928	0.638	0.842	0.906	0.930	0.665	0.645
Temp., ° F.	196	117	151	180	201	122	120
Olefin compn. in liq., mole fraction SFB[a]	0.62	0.72	0.68	0.62	0.59	0.34	0.57
Tray efficiency							
N_G	0.94	1.10	1.02	0.94	0.97	1.03	1.03
$(1/N_G)/(mV/LN_L)$	1.38	2.33	1.97	1.58	1.40	2.30	2.75
E_{OG}	0.42	0.54	0.49	0.44	0.43	0.51	0.53
L/V, SFB[a]	2.14	1.08	1.32	1.60	2.11	1.37	1.41
$A_{MS} - A_{IS}$	0.188	0.350	0.272	0.254	0.219	0.300	0.275
α_{MI}, trays 2–11	1.33	1.44	1.48	1.51	1.43	1.37	1.30
α_{MI}, without solvent	0.891	0.865	0.878	0.887	0.892	0.867	0.866

[a] Solvent-free basis.

relative volatilities differ on the average by only 5.0% from relative volatility values computed from the correlation line of Figure 6; the maximum deviation is 8.9%. The decrease in $(A_{MS} - A_{IS})$ with increasing temperature (and the corresponding decrease in α with temperature) is as expected (22).

Individual values of $(A_{MS} - A_{IS})$ were examined for the two main factors which could cause scattering of the data points:

1. Values at constant temperature were compared to determine whether any trend existed with the relative amounts of the two hydrocarbons in the liquid phase. No effect of this composition was found, indicating that solvent composition is the only composition variable which significantly affects relative volatility.
2. Values obtained from runs where the McCabe-Thiele steps were pinched were compared with values from runs where composition changes per tray were appreciable. In the former case, the magnitude of the tray efficiency had little, if any, effect on the value of relative volatility, whereas it was an important factor in the latter case. Again no trend with this variable could be found, and it was concluded that the efficiency values were sufficiently precise to permit precise calculations of relative volatility.

The correlation line (Figure 6) was then used to extend the data to other compositions and temperatures. Equation 7 was used along with the relation that $\alpha_{MI} = (\gamma_M P_M)/(\gamma_I P_I)$. The important effects of temperature and solvent concentration upon α_{MI} are clearly shown (Figure 7). For comparison, the experimental data points are shown as a function of solvent composition only in this figure. The dashed line in the figure is the locus of atmospheric boiling points shown as a function of solvent composition. Vertical deviations of the experimental points from this dashed line

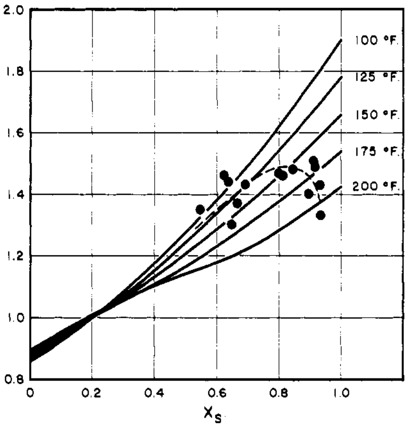


Figure 7. Solid lines show final correlation of α_{MI}, relative volatility of 2-methyl-2-butene to isoprene, as a function of dimethylformamide concentration in the liquid, x_S, and temperature

Experimental values of α_{MI} vs. x_S at 1-atm. total pressure

---- Correlation values of α_{MI} vs. x_S and temperature for operation at 1 atm.

indicate the precision of experimental data which were obtained at atmospheric pressure. These deviations averaged 5.1% and have a maximum value of 8.9%.

DISCUSSION

The volatility improvement in using dimethylformamide as an extractive agent is good. At atmospheric pressure the relative volatility of 2-methyl-2-butene to isoprene (α_{MI}) is 0.86 when no solvent is present; the value is increased to 1.27 when the solvent concentration in the liquid is 50 mole %; and it is increased to 1.50 when the solvent concentration in the liquid is increased further to 80 to 82 mole %. Above this solvent concentration, the relative volatility at 1 atm. drops because the unfavorable effect of increased temperature more than offsets the improvement effected by increased solvent concentration. This would indicate that operation at subatmospheric pressures is promising from the viewpoint of improved relative volatility. The favorable performance resulting from the use of dimethylformamide should also be realized for the separation of other olefin-diolefin pairs and for the separation of paraffin-olefin pairs.

The results of this study apply only for the case where $x_I = x_M$. Although variation in α with the x_I/x_M ratio is probably not large, the effect of this ratio upon α should be investigated more thoroughly before present data are used for design purposes.

Dimethylformamide appears attractive for use as an extractive solvent in other important respects. Its low molecular weight and high density give high molar concentrations in the liquid with low volumetric circulation rates. It is reported to be thermally stable up to 350° C., above which degradation may occur to dimethylamine and CO (*6*). It is noncorrosive (*6*) and completely misicible with water, and shows good miscibility with hydrocarbons. No phase separations were found over the concentration ranges employed in this study.

Table II. Recommended Values of Relative Volatility of 2-Methyl-2-butene to Isoprene

Solvent Concn. in Liquid, Mole Fraction	Temperature, ° F. 100	125	150	175	200
1.00	1.91	1.78	1.66	1.54	1.43
0.80	1.62	1.54	1.46	1.38	1.29
0.60	1.38	1.34	1.29	1.23	1.18
0.40	1.18	1.15	1.13	1.11	1.07
0.20	1.00	1.01	1.00	0.99	0.98
0.00	0.858	0.869	0.877	0.885	0.892

Final decision on suitability of dimethylformamide for a specific application must be made on the basis of economic considerations. Such studies are beyond the scope of the present paper, although it should be mentioned that the present cost of dimethylformamide is greater than that for some other extractive solvents now in commercial use.

Results of this study have also demonstrated the feasibility of obtaining relative volatility data for an extractive distillation system from measurements made with a pilot-scale column. Use of such an experimental procedure is often less time-consuming than use of conventional vapor-liquid equilibrium methods. The procedure has the additional advantage that the predicted tray efficiencies can be checked by making some of the tests in pinch regions where α-values are not dependent upon tray efficiencies. If such α-values check those obtained where precise efficiencies are required, the efficiencies are correct. A final advantage of the present procedure is that the operability of the extractive column is demonstrated, and preliminary information can be obtained on constancy of flow rates within the column, on reboiler and condenser heat loads and on degree of foaming on the trays.

It is not believed that data obtained from vapor-liquid equilibrium experiments should be wholly replaced by data from pilot-scale columns, but if the latter tests are performed first, a larger amount of useful information—although not as precise—is obtained. A thorough evaluation of an extractive distillation system would require data obtained by both methods.

ACKNOWLEDGMENT

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NOMENCLATURE

A_{12} = log γ_1 as $x_1 \rightarrow 0$ and $x_2 \rightarrow 1$
C^* = ternary constant in Equation 6
D = diffusivity
E = plate efficiency
F = F factor or flooding factor = $\mu\ \rho_G^{0.5}$
L = molar liquid rate
m = slope of equilibrium curve
N = number of transfer units
R = molar recycle rate
t_L = contact time of liquid on bubble tray
T = absolute temperature
u = gas rate, ft./sec. μ
V = molar vapor rate
x = mole fraction of component in liquid phase
y = mole fraction of component in vapor phase
z = mole fraction of component in recycle liquid

Greek letters

α = relative volatility = $(y_1/x_1)/(y_2/x_2)$
γ = liquid-phase activity coefficient
μ = viscosity
ρ_G = gas density, lb./cu. ft.

Subscripts

1,2 = any two components
L = liquid
G = gas
I = isoprene
M = 2-methyl-2-butene
S = solvent, dimethylformamide
MV = Murphree vapor
OG = over-all gas

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Saturation Properties and Liquid Compressibilities for Benzene and *n*-Octane

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CALCULATION of accurate thermodynamic properties of solutions at high temperature and pressure requires, among other things, precise knowledge of the properties of the pure components. In the course of correlating high pressure measurements on solutions that contained benzene or *n*-octane, gaps in the available liquid-phase properties and discrepancies in the vapor pressures were encountered.

The compressibilities of liquid benzene have been measured by Glanville (*5*) up to 237.78° C.; the rapid change with temperature does not permit extrapolation of his data to higher temperatures. Compressibilities of liquid *n*-octane have been measured by Felsing (*3*) up to 275° C., but the 25° C. spacing between isotherms makes interpolation in the high-temperature region uncertain.

Numerous measurements have been made of the vapor pressure of benzene at high temperatures. Nevertheless, two recent sets of measurements (*1, 6*) disagree by more than 1%. An independent check appears necessary. The only available high-temperature vapor pressure measurements on *n*-octane date from 1900 (*11*)

With these deficiencies in mind, four kinds of measurements have been made on benzene and *n*-octane. These measurements, made at 10° C. intervals, were:

Property	Temperature Range, ° C. Benzene	Temperature Range, ° C. *n*-Octane
Vapor pressure	130-t_c	150-t_c
Saturated vapor volume	160-280	190-280
Saturated liquid volume	130-280	190-280
Liquid compressibility	130-270	130-280

The saturation properties were used to derive heats of vaporization for benzene from 160° C. to the critical temperature and for *n*-octane from 190° C. to the critical temperature.

EXPERIMENTAL

The benzene and *n*-octane used were American Petroleum Institute standard samples with stated purities of 99.98 and 99.94 mole %. The samples arrived with magnetic break-off tips and were not exposed to air during handling. No further purification was attempted, except to remove any traces of air by distillation in vacuo. The pressure rise on going from the dew point (no liquid present) to the bubble point (no vapor present was 0.01 atm. at 200° C.

In the experimental method (*2*), a sample was confined