

LITERATURE CITED

- (1) Beattie, J. A., Kay, W. C., *J. Am. Chem. Soc.* **59**, 1586 (1937).
- (2) Boomer, E. H., Johnson, C. A., Argue, G. H. *Can. J. Research*, **B**, 15, 367 (1937).
- (3) Boomer, E. H., Johnson, C. A., Piercey, A. G. A., *Ibid.*, 396 (1938).
- (4) Bridgeman, O. C., *J. Am. Chem. Soc.* **49**, 1174 (1927).
- (5) Budenholzer, R. A., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.* **32**, 384 (1940).
- (6) Eduljee, H. E., Newitt, D. M., Weale, K. E., *J. Chem. Soc.* **1951**, 3086.
- (7) Keyes, F. G., Burks, H. G., *Ibid.*, 49, 1403 (1927).
- (8) Kvalnes, H. M., Gaddy, V. L., *Ibid.*, 53, 394 (1931).
- (9) Michels, A., Nederbragt, G. W., *Physica*, **3**, 569 (1936).
- (10) Nichols, W. B., Reamer, H. H., Sage, B. H., *Ind. Eng. Chem.* **47**, 2219 (1955).
- (11) Olds, R. H., Reamer, H. H., Sage, B. H., Lacey, W. N., *Ibid.*, 35, 922 (1943).
- (12) Reamer, H. H., Olds, R. H., Sage, B. H., Lacey, W. N., *Ibid.*, 34, 1526 (1942).
- (13) Reamer, H. H., Sage, B. H., Lacey, W. N., *Ibid.*, 41, 482 (1949).
- (14) *Ibid.*, 42, 534 (1950).
- (15) Rossini, F. D., Pitzer, K. S., Arnett, R. L., Braun, R. M., Pimentel, G. C., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, 1953.
- (16) Sage, B. H., Budenholzer, R. A., Lacey, W. N., *Ind. Eng. Chem.* **32**, 1262 (1940).
- (17) Sage, B. H., Lacey, W. N., "Some Properties of the Lighter Hydrocarbons, Hydrogen Sulfide, and Carbon Dioxide," American Petroleum Institute, New York, 1955.
- (18) Sage, B. H., Lacey, W. N., "Thermodynamic Properties of the Lighter Paraffin Hydrocarbons and Nitrogen," *Ibid.*, 1950.
- (19) Sage, B. H., Lacey, W. N., *Trans. AIME*, 136, 136 (1940).
- (20) Smith, L. B., Beattie, J. A., Kay, W. C., *J. Am. Chem. Soc.* **59**, 1587 (1937).
- (21) Vold, R. D., *Ibid.*, 57, 1192 (1935).

Received for review December 20, 1955 Accepted May 7, 1956

Ethyl Alcohol-Water with 2,2,4-Trimethylpentane and with 1-Octene at 0° and 25° C.

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In exploring the use of ethyl alcohol as a gasoline additive for preventing carburetor icing, it was desirable to obtain information on the amount of alcohol that would be extracted from the gasoline by water layer always present in the bottoms of storage tanks. The distribution of ethyl alcohol between water and the pure hydrocarbons 2,2,4-trimethylpentane and 1-octene was determined at temperatures of 0° and 25° C.

EXPERIMENTAL MATERIALS AND METHODS

2,2,4-Trimethylpentane of certified knock-rating grade was fractionated in an efficient column and, in order to remove olefins, was filtered through a long tube packed with silica gel. Its density at 25° C. was 0.68774 gram per ml. The accepted value is 0.68777 (1).

1-Octene, Phillips pure grade specified as better than 99 mole % pure, was used without further treatment. Its density was 0.71078 gram per ml. at 25° C. The accepted value is 0.71085 (1).

The commercial absolute ethyl alcohol had a density of 0.78597 gram per ml. at 25° C., corresponding to a water content of 0.30% by weight (4). This water content was taken into account in calculating the composition of the solutions.

Distilled water was taken from the laboratory supply.

The experimental procedure was adapted mainly from that used by Washburn and coworkers in their study of alcohol-water-hydrocarbon systems (8). We obtained solubility data for the ethyl alcohol-water-benzene system, not included here, which were in good agreement with those found by Washburn.

Points on the binodal curves were determined by titrating a known mixture of two components with the third component until turbidity appeared or disappeared. The mixtures were made by volume with calibrated pipets and burets, and their composition was converted to weight percent by using the densities previously mentioned. Over most of the composition range, ethyl alcohol-hydrocarbon mixtures were titrated with water. At the lower end of the water-rich part of the binodal curve, better results were obtained by titrating ethyl alcohol into a two-phase mixture

of water and hydrocarbon until a homogeneous solution was obtained.

For the 25° C. isotherm, the end point was taken as that composition which would remain homogeneous in a bath maintained at 25.0°, but would become turbid when placed in a bath maintained at 24.8° C. The titrations at 0° C. were performed in small conical flasks supported in a bath of ice and water contained in a large unsilvered Dewar vessel. The solutions were stirred with a magnetic stirring apparatus, placed next to the Dewar vessel, with its rotating magnet in the same plane as the bottom of the titration flask which contained a small magnetized stirring bar. By this arrangement, enough power was transmitted to provide adequate stirring. The solution was observed

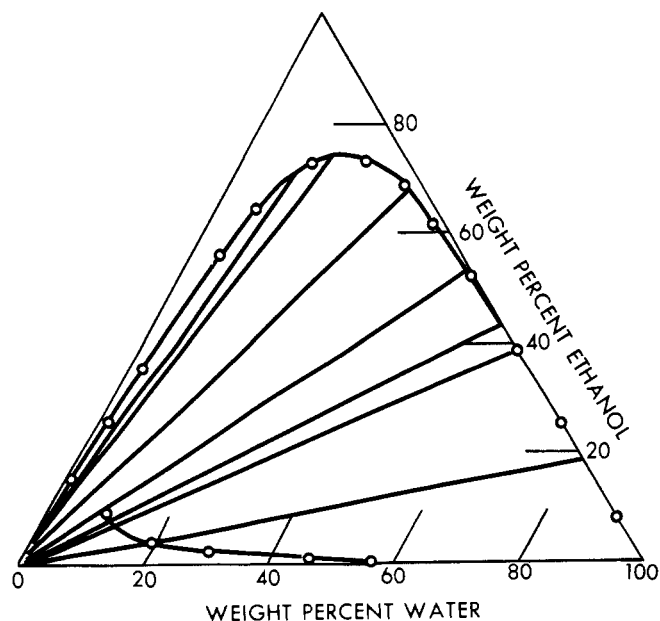
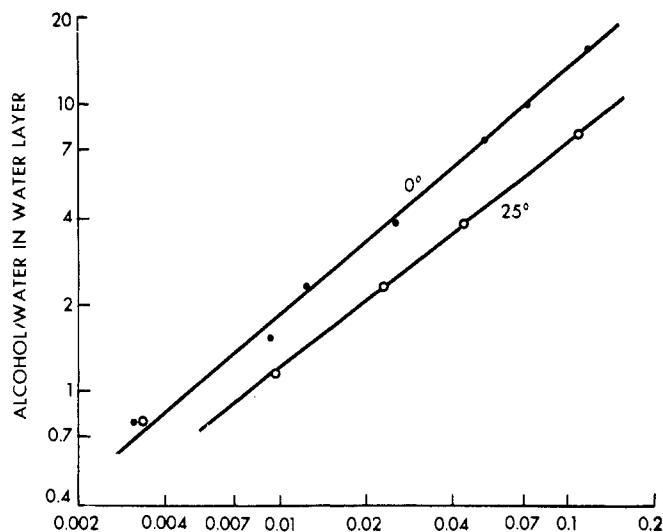


Figure 1. Triangular diagram for 2,2,4-trimethylpentane at 25° C.

through a small window cleared in the ice at the side of the Dewar vessel.

Refractive indices of the saturated solutions thus obtained were determined within 0.0002 with a Bausch & Lomb Abbe refractometer. Water from the constant-temperature bath at 25.0° C. was pumped through the prism jackets.

The tie lines were determined by making ternary mixtures which would separate into phases approximating the desired composition, then agitating them vigorously, and allowing the phases to separate at 0° or 25° C. The refractive indices of both phases were measured at 25° C., and their compositions were read from graphs of refractive index against weight percent for the saturated solutions. Along the hydrocarbon-rich sides of the binodal



ALCOHOL/WATER IN WATER LAYER

ALCOHOL/HYDROCARBON IN HYDROCARBON LAYER

Figure 2. Hand plots for 2,2,4-trimethylpentane

curves, the plots of refractive index against weight percent of ethyl alcohol were essentially straight lines which intersected the axis of zero alcohol concentration at the refractive index of the pure hydrocarbon. The slopes of these lines were such that 1% of alcohol corresponded to a change in refractive index of about 0.0003 for 2,2,4-trimethylpentane and 0.0005 for 1-octene. Since the refractive indices were measured to 0.0002, it was possible to determine alcohol concentrations in the region near 100% of hydrocarbon with errors well below 1%.

For the system involving 2, 2, 4-trimethylpentane, refractive index becomes rather insensitive to composition near the apex of the binodal curve, the region where the upper ends of most of the measured tie lines fall. For this system, the densities at 25° C. for saturated solutions containing more than 40% ethyl alcohol were measured also, and the composition of tie-line solutions in this region was determined from either their densities or refractive indices.

RESULTS AND DISCUSSION

Tables I through IV give the compositions of saturated solutions and the tie-line data. Figure 1 is the ternary diagram for the system, ethyl alcohol-water-2,2,4-trimethylpentane at 25° C., showing the binodal curve, the tie lines, and the conjugation line. The conjugation line is a plot of percent ethyl alcohol in one layer against percent water in the other layer. It intersects the binodal curve at the plait point whose location is usually determined experimentally by this fact. The shapes of the curves in Figure 1

TABLE I. ETHYL ALCOHOL-WATER-2,2,4-TRIMETHYLPENTANE AT 0° C.

Solubility Data							
Ethyl alcohol, wt. %	Water, wt. %	Refractive index, 25°		Ethyl alcohol, wt. %	Water, wt. %	Refractive index, 25°	
		n_D	Density, d_4			n_D	Density, d_4
12.2	87.8	1.3409	..	72.7	24.1	..	0.84375
25.2	74.8	1.3494	..	74.4	21.3	1.3635	..
34.9	65.1	1.3547	..	74.8	20.8	..	0.83410
37.4	62.6	1.3557	..	76.6	16.6	1.3641	..
42.1	57.8	..	0.92672	77.4	15.8	..	0.81832
45.6	54.3	1.3585	..	77.2	14.3	..	0.81220
49.1	50.7	..	0.91110	74.8	8.7	..	0.78814
49.4	50.4	1.3595	..	66.1	4.8	1.3688	..
58.1	41.4	..	0.88949	58.5	3.3	1.3710	..
59.3	40.2	1.3616	..	52.1	2.8	1.3728	..
64.3	34.6	1.3623	..	43.1	2.0	1.3751	..
64.5	34.4	..	0.87188	31.0	1.3	1.3792	..
72.4	24.4	1.3632	..	18.7	0.6	1.3829	..

Tie-Line Data

Hydrocarbon-Rich Layer			Water-Rich Layer			
Ethyl alcohol, wt. %	Hydrocarbon, wt. %	Refractive index, 25° n_D	Ethyl alcohol, wt. %	Water, wt. %	Refractive index, 25° n_D	Density, 25° d_4
0.9	99.1	1.3888	60.4	38.9	1.3617	0.88325
1.2	98.8	1.3887	68.6	29.5	1.3630	0.85909
2.4	97.5	1.3883	75.6	19.6	1.3639	0.83014
4.9	95.0	1.3875	75.7	10.2	1.3649	0.79554
6.7	93.1	1.3869	73.7	7.4	1.3660	0.78075
10.5	89.2	1.3856	62.9	4.0	1.3698	..

TABLE II. ETHYL ALCOHOL-WATER-2,2,4-TRIMETHYLPENTANE AT 25° C.

Solubility Data							
Ethyl alcohol, wt. %	Water, wt. %	Refractive index, 25°		Ethyl alcohol, wt. %	Water, wt. %	Refractive index, 25°	
		n_D	Density, d_4			n_D	Density, d_4
8.0	92.0	1.3379	..	61.9	36.7	1.3621	..
16.4	83.6	1.3438	..	68.8	28.1	..	0.85376
25.2	74.8	1.3496	..	73.3	20.2	1.3638	..
32.0	67.9	1.3532	..	73.4	20.1	..	0.82899
39.0	60.9	1.3563	..	72.8	11.2	1.3653	..
39.9	59.9	..	0.93135	72.9	11.0	..	0.79405
42.2	57.6	..	0.92641	65.2	6.2	..	0.76755
50.1	49.5	1.3597	..	64.9	6.7	1.3683	..
50.7	48.9	..	0.90675	56.8	4.7	1.3710	..
52.6	46.9	1.3603	..	36.5	2.2	1.3773	..
58.9	40.1	1.3612	..	26.7	1.4	1.3808	..
60.0	39.1	..	0.88333	15.8	0.6	1.3840	..

Tie-Line Data

Hydrocarbon-Rich Layer			Water-Rich Layer			
Ethyl alcohol, wt. %	Hydrocarbon, wt. %	Refractive index, 25° n_D	Ethyl alcohol, wt. %	Water, wt. %	Refractive index, 25° n_D	Density, 25° d_4
0.0	100.0	1.3891	38.8	61.1	1.3562	..
0.3	99.7	1.3889	43.3	56.3	1.3578	0.92348
0.9	99.0	1.3888	53.4	46.1	1.3606	0.90015
2.2	97.7	1.3884	68.0	29.2	1.3631	0.85676
4.1	95.7	1.3878	73.7	19.2	1.3640	0.82594
9.8	89.8	1.3859	70.1	9.0	1.3664	..

TABLE III. ETHYL ALCOHOL-WATER-1-OCTENE AT 0° C.

Solubility Data					
Ethyl alcohol, wt. %	Water, wt. %	Refractive index, 25 °D	Ethyl alcohol, wt. %	Water, wt. %	Refractive index, 25 °D
8.0	92.0	1.3379	65.5	33.0	1.3630
12.2	87.8	1.3409	68.4	29.6	1.3633
16.4	83.6	1.3438	75.5	17.6	1.3656
25.2	74.8	1.3495	75.0	11.5	1.3679
34.4	65.6	1.3543	73.5	9.8	1.3692
38.5	61.5	1.3560	64.9	5.8	1.3744
43.1	56.8	1.3578	50.9	3.3	1.3815
45.6	54.3	1.3585	35.0	1.8	1.3893
51.0	48.8	1.3600	18.7	0.8	1.3970
58.8	40.6	1.3618			

Tie-Line Data					
Hydrocarbon-Rich Layer			Water-Rich Layer		
Ethyl alcohol, wt. %	Hydrocarbon, wt. %	Refractive index, 25 °D	Ethyl alcohol, wt. %	Water, wt. %	Refractive index, 25 °D
0.2	99.8	1.4062	29.3	70.6	1.3518
0.5	99.5	1.4060	43.7	56.1	1.3580
0.8	99.2	1.4059	59.9	39.5	1.3620
1.8	98.2	1.4054	69.0	28.8	1.3634
2.9	97.0	1.4048	74.7	19.5	1.3651
5.9	93.9	1.4033	72.9	9.4	1.3696

are such that the plait point cannot be located by this means. The other ternary diagrams determined in this investigation are quite similar to Figure 1, and are not shown.

Consistency of the tie-line data was tested by the method of plotting suggested by Hand (2) as shown in Figures 2 and 3. The points fall on straight lines within the precision in which composition of the tie-line solutions can be determined from refractive index or density.

For the systems studied here, the solubility of hydrocarbon in the water-rich layer is considerably less than the solubility of water in the hydrocarbon-rich layer at the same alcohol concentration. The binodal curves for the two hydrocarbons are almost identical at a given temperature, although the solubility of water in the hydrocarbon-rich layer is slightly greater for 1-octene than for 2,2,4-trimethylpentane. Reducing the temperature from 25° to 0° C. enlarges slightly the area of immiscibility and increases the alcohol concentration at the apex of the binodal curve by about 3%.

The tie lines slope sharply upward towards the water-rich side of the diagram. In other words, the distribution ratio—alcohol in the water-rich layer divided by alcohol in the hydrocarbon-rich layer—is very large. In fact, water-rich solutions containing as much as 30% alcohol are in equilibrium at 25° C. with solutions that cannot be distinguished from pure 2,2,4-trimethylpentane by the refractive index measurements. The behavior of the system, ethyl alcohol-water-1-octene, is quite similar, except that the distribution ratio is somewhat smaller than it is for 2,2,4-trimethylpentane at the same temperature and alcohol concentration. These relationships can be deduced from Figures 2 and 3.

Schweppe and Lorah (5) have recently published tie-line data at 30° C. for the system, ethyl alcohol-water-n-heptane. The behavior of this system would be expected to resemble closely that of the system, ethyl alcohol-water-2,2,4-trimethylpentane at 25° C., but the results

TABLE IV. ETHYL ALCOHOL-WATER-1-OCTENE AT 25° C.

Solubility Data					
Ethyl alcohol, wt. %	Water, wt. %	Refractive index, 25 °D	Ethyl alcohol, wt. %	Water, wt. %	Refractive index, 25 °D
8.0	92.0	1.3379	63.8	34.2	1.3629
12.2	87.8	1.3408	67.6	29.3	1.3639
16.4	83.6	1.3439	71.7	23.1	1.3650
25.2	74.8	1.3494	72.3	21.1	1.3653
30.7	69.3	1.3527	72.9	17.1	1.3668
31.2	68.7	1.3529	71.7	12.1	1.3693
38.8	61.1	1.3560	63.7	7.5	1.3743
42.4	57.4	1.3574	50.0	4.7	1.3818
50.2	49.4	1.3600	34.7	2.4	1.3893
60.7	37.9	1.3621	18.0	1.1	1.3972

Tie-Line Data					
Hydrocarbon-Rich Layer			Water-Rich Layer		
Ethyl alcohol, wt. %	Hydrocarbon, wt. %	Refractive index, 25 °D	Ethyl alcohol, wt. %	Water, wt. %	Refractive index, 25 °D
0.0	100.0	1.4063	13.3	86.7	1.3415
0.4	99.5	1.4060	27.8	72.2	1.3511
0.7	99.2	1.4059	44.1	55.9	1.3580
1.4	98.4	1.4055	52.3	47.2	1.3605
2.7	97.0	1.4049	67.6	29.5	1.3638
4.7	94.9	1.4039	73.1	18.9	1.3661
6.4	93.1	1.4030	72.6	14.6	1.3680
11.0	88.1	1.4007	67.9	9.2	1.3719

obtained by these authors are in marked contrast to our data on the 2,2,4-trimethylpentane system; they indicate much smaller values of the distribution ratio. On the other hand, the distribution data obtained by Vold and Washburn (7) for the system, ethyl alcohol-water-cyclohexane at 25° C. are quite similar to those we obtained for the hydrocarbons studied in this investigation.

From previous data by two of the authors (3), A. W. Francis (6) has calculated the weight percentages for part of the hydrocarbon-rich layer for 2,2,4-trimethylpentane. These data are in perfect agreement with the results of this investigation.

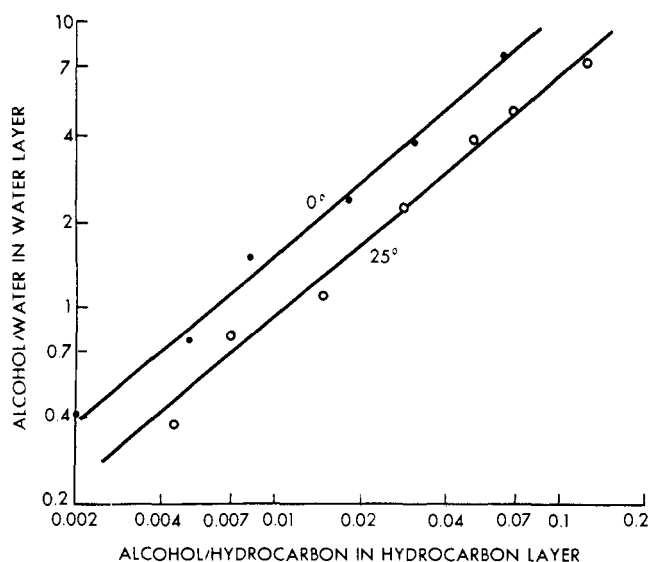


Figure 3. Hand plots for 1-octene

LITERATURE CITED

- (1) Am. Petroleum Inst. Research Project 44, "Selected Values of Properties of Hydrocarbons," Tables 3a, 10a, Carnegie Institute of Technology, Pittsburgh, 1952.
- (2) Hand, D. B., J. Phys. Chem. 34, 1961 (1930).
- (3) Kretschmer, C. B., Wiebe, Richard, Ind. Eng. Chem. 37, 1130 (1945).
- (4) Osborne, N. S., McKelvey, E. C., Bearce, H. W., Bull. Bur. Standards 9, 424 (1913).
- (5) Schweppe, J. L., Lorah, J. R., Ind. Eng. Chem. 46, 2391 (1954).
- (6) Seidell, Atherton, Linke, W. F., sections by Bates, R. G., Francis, A. W., "Solubilities of Inorganic and Organic Compounds," 3rd ed. suppl., Van Nostrand, New York, 1952.
- (7) Vold, R. D., Washburn, E. R., J. Am. Chem. Soc. 54, 4217 (1932).
- (8) Washburn, E. R., Hnizda, V., Vold, R., J. Am. Chem. Soc. 53, 3237 (1931).

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Received for review October 22, 1955 Accepted March 9, 1956

Equilibrium Vaporization Ratios Hydrocarbon Mixture Containing Two Concentrations of Heptanes and Heavier Fraction

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Equilibrium vaporization ratios have been obtained for the components, methane through heptanes-plus, in two combined natural gas-crude oil mixtures of a common source. The mixtures contained 20.13 and 11.20 mole % of heptanes-plus with relative amounts of the remaining components held constant. The data were obtained at 190° F. and cover a pressure range of 1000 to 6000 pounds/square inch.

The results of this investigation are compared with those of related work. A brief description of the apparatus and procedures used are included.

Generalized equilibrium vaporization-ratio (K value) charts, applicable to the light hydrocarbons for pressures up to 600 pounds/square inch and based on the early work of Brown (17), Katz (8), and Sage (16) are available in the literature and various handbooks. Subsequent work by Katz (9), who used a 225 molecular weight crude oil, showed the behavior of equilibrium ratios at pressures above 1000 pounds/square inch to be theoretically unpredictable. The over-all composition of these mixtures varied as the pressure was decreased to reproduce the depletion behavior of an oil reservoir.

Webber (20) reported equilibrium ratios resulting from an investigation of a natural gas-absorber oil system. The gas-oil ratio of Webber's system increased with pressure. Subsequently Eilerts (3) pointed out the importance of holding the over-all composition constant, particularly with respect to the heptanes-plus fraction. Similar data have been reported by Kirkbride and Bertetti (10).

Roland, Smith, and Kaveler (14) obtained equilibrium ratio data for gas-distillate mixtures of 50, 75, 85, and 90 mole % methane at 40°, 120°, and 200° F. Isothermal comparison of the data for the various mixtures showed that, for this particular system, the effect of varying over-all composition was not large.

Standing and Katz (18) presented considerable volumetric data on four natural gas-gasoline-crude oil mixtures. Two mixtures had sufficient equilibrium ratio data to make an isothermal-isobaric comparison at 200° F. The relative amounts of methane, ethane, and propane in these mixtures were held constant. The gas-oil ratios of the mixtures were 7180 and 3660 cubic feet per barrel.

Roland (13) investigated a fixed gas-oil ratio, natural gas-crude oil system at 120° and 200° F. over a pressure range of 1000 to 9500 pounds/square inch. Data were also given for nonfixed gas-oil ratio mixtures and a mixture derived from a high pressure vapor phase.

More recent experimental work (5, 6, 12, 19) has been concerned with equilibrium ratios for the non-hydrocarbons, nitrogen, carbon dioxide, and hydrogen sulfide in natural gas-crude oil and natural gas-distillate systems. These components, often occurring in natural petroleum reservoir mixtures, are of considerable interest and pose special analytical and experimental problems.

The amount of published experimental data on the heptanes-plus fraction, compared with those on lighter hydrocarbons, was found to be limited (1). Hence, the primary object of this investigation was to show the effect of varying the amount of heptanes-plus components while holding the relative amounts of the other components constant. Most of the previous investigators varied the composition by changing the gas-oil ratio. If the fluids used to make up the mixtures contained components which were common to both fluids, the relative amounts of these components would not remain constant in the resulting mixtures. In this investigation the mixtures were recombined in such a manner that this effect would be eliminated.

The data obtained may be divided into two groups: in the first, the liquid and gas samples were recombined in a fixed gas-oil ratio; the second group was handled in the same manner, except that the number of moles of heptanes-plus component per mole of the remaining components was decreased by a factor of one-half. Since this investigation was mainly concerned with the effects of the heptanes-plus fraction, special attention was paid to this component in analyzing the various phase samples.

MATERIALS USED

The reservoir materials used to make up the recombined equilibrium mixtures A and B in Table I were obtained from a Chitwood-Boatwright sand unit in Grady County, Oklahoma. The liquid sample was taken from a high-pressure separator operating at 98° F., and 357.3 pounds/square inch. The gas samples were taken at the same pressure from another point in the same field.

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