187.74, corresponding approximately to a normal paraffin of 13 carbon atoms. The kinematic viscosity of *n*-tridecane at 20° C. is 2.466 centistokes, significantly greater than the experimental value for the solution, 1.85 centistokes. Therefore, a solution of hydrocarbons differing widely in molecular weight may have a viscosity greater than that of a single hydrocarbon with the same weight average or "number average" molecular weight as the solution.

The agreement between the properties of solution 16, an equimolar mixture of *n*-octane and *n*-decane, and the analogous "chemical mixture" (20), *n*-nonane, supports the conclusion that the excess viscosity of the hexane-hexadecane solution is due to the large difference between the molecular weights of the components.

Solutions 13 and 14 further illustrate the molecular weight effect. Each of these solutions is composed of 1,2-dicyclohexylethane and a *n*-paraffin in equimolar proportions. In solution 13 the *n*-paraffin component is *n*-hexane, and there is a very significant difference in the molecular weights of the two components. As a result, there is no congruence between the properties of the "physical mixture," solution 13, and the corresponding chemical mixture, 1-butylcyclohexane (17).

In contrast, the *n*-paraffin present in solution 14 is *n*-tetradecane and thus the molecular weight disparity between the two components is of the order of 1%. The correspondence between the physical properties of solution 14 and the chemical mixture, *n*-octylcyclohexane (18), is excellent.

## ACKNOWLEDGMENT

The generous support of the Research Corp. and the American Petroleum Institute is gratefully acknowledged.

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RECEIVED for review June 19, 1958. Accepted February 25, 1959. Division of Petroleum Chemistry, 129th Meeting, ACS, Dallas, Tex., April, 1956.

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# Solubility of 1,3-Butadiene in Water

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This paper reports the solubility of 1,3-butadiene in water at pressures to 275 p.s.i.a. A summary of the light hydrocarbon-water systems studied to date is presented in Table I.

Three isotherms were investigated: 100°, 160°, and 220°F, with pressures ranging from the vapor pressure of water to the pressure at which a hydrocarbon-rich liquid phase appeared. The rocking autoclave equipment with its sampling device, which enables liquid samples to be taken under constant pressure, is identical to that used in earlier studies (*1*).

The experimental and smoothed data are shown in Tables

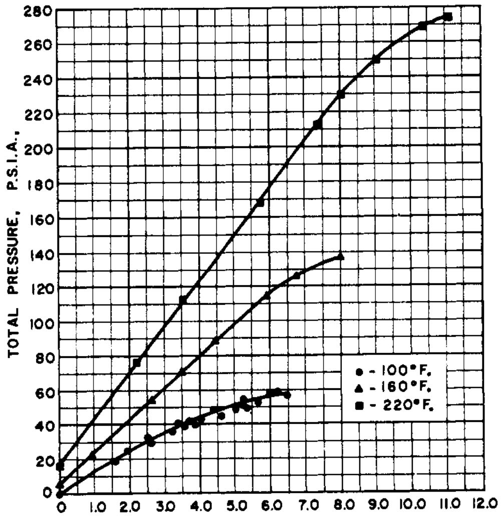

Figure 1. Concentration of 1,3-butadiene in water-rich liquid phase region *vs.* total pressure

Table I. Light Hydrocarbon-Water Systems

| System | Phases Reported$^a$ | Temp., ° F. | Maximum Conditions<br>Pressure, p.s.i.a. | Ref. |
|---|---|---|---|---|
| $CH_4$-$H_2O$ | W | 77 | 2,350 | (*13*) |
|  | W | 340 | 10,000 | (*9, 10, 19*) |
|  | V | 460 | 10,000 | (*20*) |
| $C_2H_6$-$H_2O$ | W | 340 | 1,200 | (*7*) |
|  | W and V | 340 | 10,000 | (*8, 10*) |
|  | *P* and *T* data | 89 | 710 | (*17*) |
|  | V | 303.7 | 1,000 | (*23*) |
| $C_2H_4$-$H_2O$ | W | 100 | 7,350 | (*3*) |
|  | *P* and *T* data | 68 | 882 | (*11, 12*) |
|  | V | 68 | 570 | (*12*) |
| $C_2H_2$-$H_2O$ | W | 86 | 570 | (*15*) |
| $C_3H_8$-$H_2O$ | 3- and 2-phase regions | 340 | 3,000 | (*16*) |
|  | H and V | 187 | 500 | (*22*) |
|  | V | 100 | 192 | (*21*) |
|  | V | 70 | 120 | (*14*) |
|  | W | 220 | 500 | (*1*) |
| $C_3H_6$-$H_2O$ | W | 220 | 500 | (*2*) |
| *n*-$C_4H_{10}$-$H_2O$ | 3-phase region | 460 | 10,000 | (*24*) |
|  | 3- and 2-phase regions | 220 | 10,000 | (*4, 25*) |
| $C_4H_8$-$H_2O$ | 2- and 3-phase regions | 220 | 10,000 | (*18*) |
|  | W | 291 | 1,000 | (*5*) |
|  | H | 291 | 1,000 | (*6*) |
| i-$C_4H_{10}$-$H_2O$ | W | 220 | 315 | (*26*) |
| $C_4H_6$-$H_2O$ | W | 220 | 276 | (This work) |

$^a$W = water-rich liquid. H = hydrocarbon-rich liquid. V = vapor.

II and III, respectively, and in Figure 1. Reproducibility of the data was very good at 220° and 160° F. and it was fair in the 100° F. isotherm.

The accuracy of the two higher isotherms is believed to be within 2% of the true values and of the lower, within 5%. The greater deviations in the 100° F. isotherm are due to accumulative errors in the repeated flashing of the liquid sample to determine the dissolved butadiene.

### Table II. Experimental Data in Two Phase Region

(Concentration of 1,3-butadiene in water-rich liquid phase)

| 100° F. | | 160° F. | | 220° F. | |
|---|---|---|---|---|---|
| Total pressure, p.s.i.a. | Mole fraction × $10^5$ | Total pressure, p.s.i.a. | Mole fraction × $10^5$ | Total pressure, p.s.i.a. | Mole fraction × $10^5$ |
| 58.9 | 62.5 | 137.7 | 80.4 | 275.7 | 111.9 |
| 58.0 | 60.0 | 126.7 | 67.3 | 269.2 | 104.6 |
| 57.6 | 65.0 | 114.7 | 59.4 | 251.7 | 90.1 |
| 55.7 | 52.8 | 88.7 | 44.7 | 230.7 | 80.8 |
| 50.6 | 52.6 | 70.7 | 34.9 | 212.7 | 72.8 |
| 49.6 | 53.7 | 54.9 | 26.9 | 168.2 | 57.5 |
| 48.6 | 43.6 | 22.7 | 9.5 | 111.7 | 35.7 |
| 45.3 | 46.3 | | | 76.7 | 22.3 |
| 43.7 | 40.6 | | | | |
| 42.2 | 37.1 | | | | |
| 40.3 | 34.11 | | | | |
| 40.0 | 38.8 | | | | |
| 39.0 | 35.8 | | | | |
| 37.1 | 32.5 | | | | |
| 32.9 | 25.4 | | | | |
| 29.7 | 26.6 | | | | |
| 25.2 | 19.8 | | | | |
| 19.1 | 16.3 | | | | |

### Table III. Smoothed Data on Two-Phase Region

(Concentration of 1,3-butadiene in water-rich liquid phase)

| 100° F. | | 160° F. | | 220° F. | |
|---|---|---|---|---|---|
| Total pressure, p.s.i.a. | Mole fraction × $10^5$ | Total pressure, p.s.i.a. | Mole fraction × $10^5$ | Total pressure, p.s.i.a. | Mole fraction × $10^5$ |
| 0.97[a] | 0 | 4.7[a] | 0 | 17.2[a] | 0 |
| 10 | 8.0 | 10 | 3.0 | 20 | 1.0 |
| 20 | 16.0 | 20 | 8.5 | 40 | 8.6 |
| 30 | 25.4 | 40 | 19.0 | 60 | 16.1 |
| 40 | 35.5 | 60 | 29.5 | 80 | 23.6 |
| 50 | 48.0 | 80 | 40.0 | 100 | 31.2 |
| 55 | 57.5 | 100 | 51.0 | 120 | 39.0 |
| | | 120 | 62.8 | 140 | 46.5 |
| | | 130. | 70.6 | 160 | 58.0 |
| | | 138.5 | 80.0 | 180 | 61.5 |
| | | | | 200 | 69.0 |
| | | | | 220 | 76.3 |
| | | | | 240 | 85.0 |
| | | | | 260 | 96.5 |
| | | | | 270 | 105.0 |
| | | | | 275 | 111.5 |

[a] Vapor pressure of water.

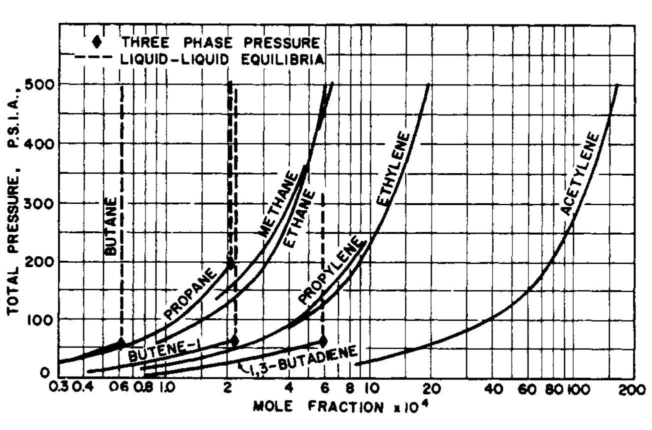

Figure 2. Comparison of solubility of various hydrocarbons in liquid water at 100° F.

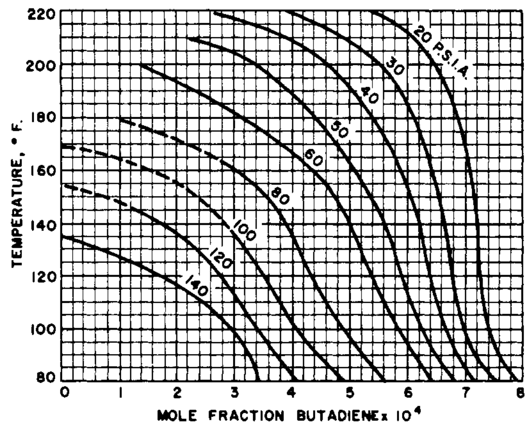

Figure 3. Temperature-composition diagram of butadiene–water in the water-rich liquid region

A correction for the inclusion of water vapor was applied to all analyses, but at the higher isotherms, where the solubility was greater, this corrective factor was not as significant as in the lower runs.

A comparison of the solubility of 1,3-butadiene with various other hydrocarbon-water systems is shown in Figure 2.

A temperature-composition diagram is shown in Figure 3. 1,3-Butadiene does not exhibit the minimum solubility phenomenon that is typical of other hydrocarbon-water systems. A minimum may occur outside this temperature range.

## ACKNOWLEDGMENT

The authors acknowledge the assistance of the Phillips Petroleum Co. in providing the research grade 1,3-butadiene used. This work was carried out under a National Science Foundation Grant.

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Received for review March 10, 1959. Accepted March 27, 1959.