# Effects of Freezing Point Depression on Molecular Weight Determination of Hydrocarbon Mixtures.

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## ABSTRACT

The molecular weight of components of four hydrocarbon mixtures n-Nonane+n-Tetradecane, n-Hexane+n-Nonane, n-Hexane+Toluene, and Toluene+n-Tetradecane were determined by an experimental procedure based on freezing point depression. The results showed a marked improvement from the values obtained using the Kay's mixing rule, for the molecular weight determination of multicomponent mixtures. The results also form the bases for the determination of the critical properties of hydrocarbon mixtures.

(Keywords: freezing point depression, hydrocarbon mixtures, mixing rule, molecular weight)

## INTRODUCTION

Molecular weight determination of hydrocarbon fluids is very important for the accurate estimation of thermodynamic properties [1], [2], [3], [4]. Petroleum reservoir fluids consist of thousands of different components, hydrocarbons and hetero-components. These components possess a wide range of boiling point and molecular weight, [5]. [6] noted that the second step in characterization of plus fractions, of multicomponent petroleum mixtures involves use of estimated specific gravity and molecular weight to estimate critical properties required by equation of states.

According to [7] accurate estimation of mixtures depends on the estimation of properties of pure compound in the mixture. The molecular weight estimates can be easily obtained for a pure component, unlike those of binary and multicomponent hydrocarbon mixtures which are usually obtained by the application of mixing rule [8], [5], [9].

Mixing rules are important in the characterization of reservoir fluid as it is used in the development equation of state and development of critical properties. Reservoir fluids are always composed of lighter gaseous / liquid component and heavier (more solid C7+ components) and other heavier components which are lumped together to form as pseudo components. Kay's rule [10] is the commonly used to determine the molecular weight and properties of these multicomponent fluids, properties are obtained by summing the products of the component and the relative molar fraction for the group of components in a multicomponent mixture.

Since estimates are used to determine the molecular weight of binary and multicomponent mixture, there are bound to be errors as the number of components in a mixture increase. Numerous inaccuracies results when using kay's mixing rule for real fluids [11]; therefore, there is need for an accurate method of molecular weight determination for multicomponent fluids. A number of techniques are available for the determination of molecular weight of hydrocarbons, these are based on the principle of boiling point elevation, freezing point depression, vapor phase osmosis or chromatography, and they further pointed out that freezing point depression still remains the most preferred [12].

Freezing point depression is a colligative property, along with vapor pressure lowering, boiling point elevation and osmotic pressure it utilizes the theory of concentration determination by freezing point and is defined as the difference between the freezing point of solvent and the freezing point of solution of the solvent and solute. There is a linear relationship between the freezing point depression constant ($K_f$) of a solvent, the concentration of the sample and

freezing point depression. The freezing point depression varies for different pure solvents with $K_f$ of water at $1.86^oC/mol$ and benzene at $5.12^oC/mol$. The $K_f$ varies slightly with the concentration of sample and decrease with increasing concentration.

## PREPARATION OF MIXTURES

Mixtures were prepared from the pure components in nine different proportions, four mixtures were prepared which includes: Hexane + n-Nonane; Hexane + Toluene; Toluene + n-Tetradecane; n-None + n-Tetradecane; the total weights of mixture were 0.889g, the pure components were purchased from commercial sources, since the pure components where all soluble in benzene, benzene was used as the pure solvent. The pure component where used without further purification the goal was to measure the freezing point depression $\Delta F_p$ of the pure component mixtures

The CRYETTE WR was used to determine the freezing point depression of various mixture and thereafter their molecular weight was determined.

## METHODOLOGY

Mixtures of pure components were prepared with various proportions of the pure component in the mixture. The freezing point depression of the pure components and binary mixture were measured using the CRYETTE Osmometer. The molecular weight of the mixture was then determined using the equation.

$$Mw = \frac{weight\ of\ solute * 1000 * K_f}{weight\ of\ solvent * \Delta F_p} \qquad (1)$$

## EXPERIMENTAL PROCEDURE

The calibration was done by putting 2.5ml of benzene in a glass tube, the bath temperature control was set at 681 in other to get a bath temperature of $1.5^oC$. The benzene sample was charged into the refrigerator well when the bath temperature indicator light blinked at $1.5^oC$. The operate switch was set at operate position, while the pure solvent Benzene froze at $1000^oC$ (i.e. display light shows 1000 after cycling).

The range was then adjusted to 000 and a second benzene sample is charged in and the $\Delta Fp$ is read.0.882g of Nonane was dissolved in in 42g of Benzene and 2.5ml of the solution was put in a glass test tube, the same procedure as that of pure component was used to determine the $\Delta Fp$ the value was found to be 845. 4 binary mixtures was then prepared at different proportions of mole fraction ranging from 0.1 to 0.9 for each binary mixture, the same procedure for pure components was used to determine the molecular weight of each binary mixtures.

## RESULTS

The Kay's (1936) mixing rule for calculating the molecular weight of mixtures was of the most comprehensive and useful in this study. Mole fraction and molecular weight was reported for the binary mixtures, the experimental, and calculated results of molecular weight of binary mixtures, at different mole fractions for pure components and their binary systems are listed in Tables 1-4.

**Table 1:** Molecular Weight Results of Nonane (1) +Tetradecane (2) System for Experimental and Kay's Mixing Rule.

| Weight (g) of Nonane (1) | Weight (g) of Tetradecane (2) | $\Delta F_p$ Milli-$^oC$ | Experimental Result (1) +(2) | Kay's mixing Rule |
|---|---|---|---|---|
| 0 | 0.889 | 546 | 198.485 | 198.4 |
| 0.0889 | 0.8001 | 549 | 197.401 | 191.386 |
| 0.1778 | 0.7112 | 600 | 180.622 | 184.372 |
| 0.2667 | 0.6223 | 608 | 178.245 | 177.358 |
| 0.3556 | 0.5334 | 576 | 188.148 | 170.344 |
| 0.4445 | 0.4445 | 648 | 167.242 | 163.33 |
| 0.5334 | 0.3556 | 709 | 152.853 | 156.316 |
| 0.6223 | 0.2667 | 720 | 150.518 | 149.302 |
| 0.7112 | 0.1778 | 758 | 142.972 | 142.288 |
| 0.8001 | 0.0889 | 823 | 131.680 | 135.274 |
| 0.889 | 0 | 845 | 128.252 | 128.260 |

**Table 2:** Molecular Weight Results of Hexane (1) + Nonane (2) System for Experimental and Kay's Mixing Rule.

| Weight (g) of Hexane (1) | Weight (g) of Nonane (2) | $\Delta F_p$ Milli-$^{0}$C | Experimental Result (1)+(2) g/mol | Kay's Mixing Rule |
|---|---|---|---|---|
| 0 | 0.889 | 845 | 128.252 | 128.26 |
| 0.1778 | 0.7112 | 930 | 116.530 | 119.844 |
| 0.3556 | 0.5334 | 905 | 119.749 | 111.428 |
| 0.5334 | 0.3556 | 1070 | 101.283 | 103.012 |
| 0.7112 | 0.1778 | 1121 | 96.675 | 94.596 |
| 0.889 | 0 | 1257 | 86.215 | 86.18 |

**Table 3:** Molecular Weight Results of Hexane (1) + Toluene (2) System, for Experimental and Kay's Mixing Rule.

| Weight (g) of Hexane (1) | Weight (g) of Toluene (2) | $\Delta F_p$ Milli-$^{0}$C | Experimental Result (1) +(2) | Kay's Mixing Rule |
|---|---|---|---|---|
| 0 | 0.889 | 1176 | 92.154 | 92.140 |
| 0.178 | 0.711 | 1235 | 87.751 | 90.948 |
| 0.356 | 0.533 | 1126 | 96.246 | 89.756 |
| 0.533 | 0.355 | 1315 | 82.413 | 88.564 |
| 0.711 | 0.177 | 1230 | 88.108 | 87.372 |
| 0.889 | 0.000 | 1257 | 86.216 | 86.180 |

**Table 4:** Molecular Weight of Results of Toluene (1) + Tetradecane (2) System, for Experimental and Kay's Mixing Rule.

| Weight (g) of Hexane (1) | Weight (g) of Toluene (2) | $\Delta F_p$ Milli-$^{0}$C | Experimental Result (1) +(2) | Kay's Mixing Rule |
|---|---|---|---|---|
| 0 | 0.889 | 1176 | 92.154 | 92.140 |
| 0.178 | 0.711 | 1235 | 87.751 | 90.948 |
| 0.356 | 0.533 | 1126 | 96.246 | 89.756 |
| 0.533 | 0.355 | 1315 | 82.413 | 88.564 |
| 0.711 | 0.177 | 1230 | 88.108 | 87.372 |
| 0.889 | 0.000 | 1257 | 86.216 | 86.180 |

## DISCUSSION OF RESULTS

Figures 1-4 were plotted from the Tables 1-4 above so that the variations can be established from the research work and the literature using the existing theories and mixing rules. In Figures 1- 4 the plots followed a similar pattern for all the plots, all the experiments were conducted at room temperature.

The plot of the experimental data and that of this study show great similarity with very slight deviation in Figures 2 and 3 while the Kay's mixing rule value deviated greatly for all the four plots, generally since the molecular weight decreased with increasing mole fraction for all the four plots, it can be stated that there was an inverse relationship between the molecular weight and the mole fraction.

Significant deviations in the experimental molecular weight from the calculated molecular weight for the four binary systems performed at room temperature from this work implies that the Kay's mixing rule does not give accurate results for molecular weight of mixtures. Experimental molecular weight of the four binary systems did not change and therefore is superior to the estimated result
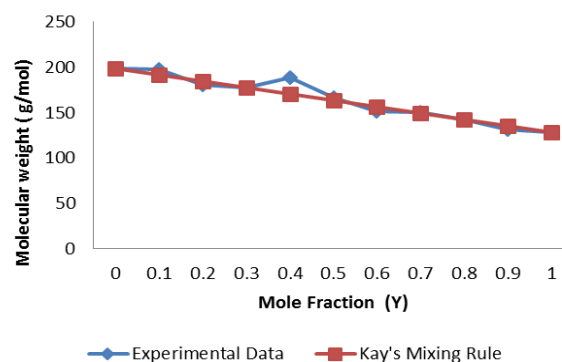


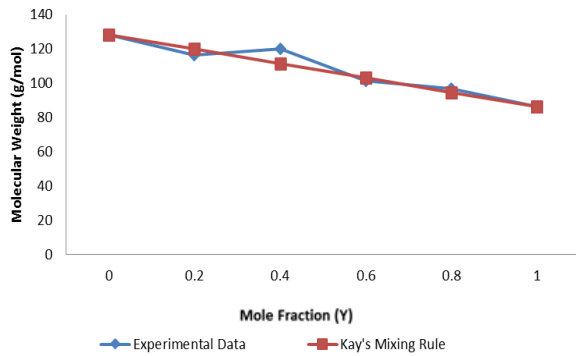**Figure 1:** Comparison of the Molecular Weight of Tetradecane (1) + Nonane (2) System.

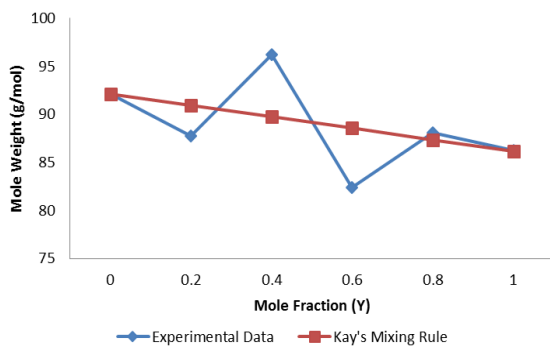**Figure 2:** Comparison of the Molecular Weight of Hexane (1) + Nonane (2) Binary System.



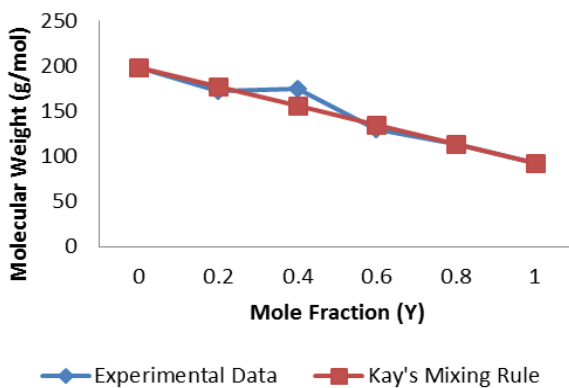**Figure 3:** Comparison of Molecular Weight of Hexane (1) + Toluene (2) Binary System.



**Fig. 4:** Comparison of molecular weight of Toluene (1) + Tetradecane (2) Binary System.

## CONCLUSION

The results show that the Kay's Mixing rule does not replicate accurately the measured values obtained from the mixtures and therefore not reliable for measuring critical properties from molecular weight. A new correlation can be developed for determining the molecular weight of mixtures. This method will have an improvement over the Kay's mixing rule and give more accurate value. Instead of limiting studies to binary mixtures, research should be extended to multicomponent systems and heavy hydrocarbon systems.

More studies should be carried out using other methods of molecular weight determination by experimental methods other than freezing point depression.

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