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EXPERIMENTAL DETERMINATION OF THE MOLECULAR WEIGHT OF SOME BINARY MIXTURES AND PETROLEUM LIQUIDS

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ABSTRACT

Accurate molecular weights of pure compounds are available and can be readily obtained in the literature. However, those of binary and multi-component mixtures are not readily available and are usually obtained from pure components by applying mixing rules, which may not be very accurate. The molecular weights of n-Nonane+n-Tetradecane, n-Hexane+n-Nonane, n-Hexane+Toluene, Toluene+n-Tetradecane and some petroleum liquids were experimentally determined using a cryoscope. The results were compared with estimates from Kay's mixing rule and the observed deviations used to modify Kay's equation in order to obtain an improved mixing rule for the molecular weight of binary mixtures. A simple relation was also established for predicting molecular weight of petroleum liquids from API gravity. The average absolute deviation (AAD) of 0.04 and 0.40 for the molecular weight of heavy and light petroleum liquids respectively represents an improvement over most of the existing correlations.

Keywords: Petroleum liquids, binary mixtures, molecular weight, mixing rule, freezing point depression.

INTRODUCTION

The molecular weight of hydrocarbon gases and liquids is very important in reservoir fluid characterization and compositional simulation. The accuracy of physical properties of hydrocarbon systems is known to affect the equation of state predictions and thermodynamic models (Whitson, 1984; Horstmann *et al.*, 2000). While accurate estimates of the molecular weights of pure compounds are available in the literature and can be readily obtained, those of binary and multi-component mixtures are not and are usually obtained from pure components by applying appropriate mixing rules. When measured in the laboratory, the molecular weights of mixtures are known to be different from values obtained using 'equivalent fluid' principles by mixing pure components. Therefore, while the molecular weights of the pure components of a mixture are available, the estimated value for the complete fluid could be inaccurate. Similarly, a very accurate value of the molecular weight of a binary or complex fluid could be available, while those of the fractions could be unreliable because of the mixing rule.

Gabito *et al.* (2003) have noted that the problems associated with representing poly-disperse mixtures such as petroleum liquids are associated with the computation of average molecular weights. Kreglewski (1967) observed that the commonly used Kay's mixing rule is not very accurate for real fluids. Several theoretically-based mixing rules have been published in the literature (Panagiotopoulos and Reid, 1985; Wong and Sandler, 1992). However, Isehunwa and Falade (2007) proposed using experimental values by 'matching' the actual measured values with the 'equivalent fluid' obtained from the mixing of pure components. They suggested a simple modification of Kay's (1936) mixing rule using a substance-dependent adjustment factor obtained by trial and error. This study was aimed at improving modification of Kay's rule in binary and multicomponent hydrocarbon liquids without recourse to trial and error.

MATERIALS AND METHODS

Pure components and Petroleum mixtures with purity above 99% were obtained from different suppliers as shown in table 1.

Table 1. Properties of Pure components and Mixtures.

Substance	Supplier	Purity (%)
Benzene	BDH Chemicals	99+
n-Hexane	BDH Chemicals	99+
n-Nonane	Aldrich Chemicals	99+
n-Tetradecane	Aldrich Chemicals	99+
Toluene	BDH Chemicals	99+
DPK	AP, NNPC	99+
AGO	AP, NNPC	99+
Crude Oil	NPDC	99+

Calibration of the Cryette WR cryoscope model 5009 was done using 2.5 ml of pure benzene (42g) as solvent at the

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bath temperature of 1.5°C. Binary mixtures were prepared at different proportions of pure components. The specific gravity of all the pure liquids, binary mixtures, petroleum and petroleum products were determined using a hydrometer and converted to API gravity. The molecular weights of the liquids were determined from the cryoscope readings using equation (1):

$$MW = \frac{\text{Weight of solute} \times 1000 \times K_f}{\text{Weight of solvent} \times \Delta FP} \quad (1)$$

Where, ΔFP is the meter reading (observed freezing point depression).

All readings were replicated three times and average values taken as the representative value.

The measured molecular weight of the binary mixtures and petroleum compounds were compared with estimated values using Kay's mixing rule and an equation was developed to relate the two. An equation was also developed to establish a relationship between the API gravity and molecular weight of the multi-component hydrocarbons.

RESULTS AND DISCUSSION

Tables 2-5 show the experimentally determined freezing point depressions and molecular weights of various for pure components and different binary mixtures. The values obtained for the pure components were chosen as control points and they generally agree with published results in the literature. Table 6 shows the measured API gravity and molecular weights of the petroleum and petroleum products. The API gravity ranged between 13 and 38, indicating rather 'heavy' liquids.

Table 2. Freezing Point Depressions and Molecular Weights of Nonane (1) + Tetradecane (2).

Mole fraction (1)	Mole fraction (2)	ΔFP milli-°C	Molecular Weight
0.0	1.0	546	198.49
0.1	0.9	549	197.40
0.2	0.8	600	180.62
0.3	0.7	608	178.25
0.4	0.6	576	188.15
0.5	0.5	648	167.24
0.6	0.4	709	152.85
0.7	0.3	720	150.52
0.8	0.2	758	142.97
0.9	0.1	823	131.68
1.0	0.0	845	128.25

Table 3. Freezing Point Depression and Molecular Weights of Hexane (1) + Nonane (2).

Mole fraction (1)	Mole fraction (2)	ΔFP milli-°C	Molecular Weight
0.0	1.0	845	128.25
0.2	0.8	930	116.53
0.4	0.6	905	119.75
0.6	0.4	1070	101.28
0.8	0.2	1121	96.68
1.0	0.0	1257	86.22

Table 4. Freezing Point Depression and Molecular Weight of Hexane (1) + Toluene (2).

Mole fraction (1)	Mole fraction (2)	ΔFP milli-°C	Molecular Weight
0.0	1.0	1176	92.15
0.2	0.8	1235	87.75
0.4	0.6	1126	96.25
0.6	0.4	1315	82.41
0.8	0.2	1230	88.11
1.0	0.0	1257	86.22

Table 5. Freezing Point Depression and Molecular Weight of Toluene (1) + Tetradecane (2).

Mole fraction (1)	Mole fraction (2)	ΔFP milli-°C	Molecular Weight
0.0	1.0	546	198.49
0.2	0.8	632	171.48
0.4	0.6	623	173.95
0.6	0.4	835	129.79
0.8	0.2	958	113.12
1.0	0.0	1176	92.15

Table 6. Freezing Point Depression and Molecular Weight of Some Complex Hydrocarbons.

Liquid	API Gravity	ΔFP milli-°C	Molecular Weight
AGO (NNPC)	12.89	489	221.62
AGO (AP)	14.38	484	223.91
DPK (NNPC)	23.99	711	152.42
DPK (AP)	25.72	667	162.48
Crude Oil (NPDC)	38.44	937	115.66

For the binary mixtures, the measured molecular weights were compared with estimates from Kay's mixing rule given as:

$$M = \Sigma y_i M_i \quad (2)$$

If we assume the molecular weight obtained using Kay's mixing rule is Meq, while the actual (measured) value is M, then the modified Kay's mixing rule can be obtained

from the deviations, using the approach of Isehunwa and Falade (2007) as:

$$M = [1 + \quad y_i (1 - y_i)] M_{eq}$$

Where,
M = Actual molecular weight measured.
M_{eq} = Molecular weight obtained from Kay's mixing rule
y_i = Mole fraction of component *i*.
M_i = Molecular weight of component *i*.
= Component-dependent empirical constant.

Equation (3) represents an improvement on the Isehunwa-Falade adjustment factor that was obtained by trial-and-error. The empirical constants developed from the deviation of the Kay's equivalent fluid from the actual fluid are presented in Table 7. Given mole fractions and molecular weights of pure components, the actual molecular weights of binary mixtures can be obtained from the equation. Tables 8-11 show the comparison of measured values and estimates from equations (2) and (3). The measured molecular weight of the petroleum and petroleum products was statistically correlated to the API gravity to obtain the relationship defined by equation (4):

$$M = 256 - 3.65API \quad (3)$$

Equation (4) was validated with data from several Niger Delta reservoirs published by Isehunwa and Falade (2007) and compared with the Cragoe (1929), Standing (1977) and Isehunwa-Falade relations described by equations (5) – (7):

Cragoe's correlation:
$M_w = 6084/ (API-5.9)$ (5)

Standing's correlation:
$M_w = 239-2.2\ API$ (6)

Isehunwa and Falade's correlation:
$M_w = 9260.1\ (API)^{-1.2894}$ (7)

Table 12 shows the AAD obtained by applying the correlations to Niger Delta reservoir data published by Isehunwa and Falade (2007). This study provided very accurate predictions for heavy crude and petroleum products (API < 32) and better predictions for light

Table 7. Mole fraction dependent empirical constants.

y_i	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
	0.00	0.35	-0.13	0.02	0.44	0.10	-0.09	0.04	0.03	-0.30	0.00

Table 8. Comparison of Experimental and Estimated Molecular Weights for Nonane (1) + Tetradecane (2) Mixtures.

Mole fraction (1)	Molecular weight		
	Experimental	Kay's Rule	This study
0.0	198.49	198.40	198.40
0.1	197.40	191.39	197.41
0.2	180.62	184.37	180.54
0.3	178.25	177.36	178.25
0.4	188.15	170.34	188.33
0.5	167.24	163.33	167.25
0.6	152.85	156.32	152.86
0.7	150.52	149.30	150.52
0.8	142.97	142.29	142.97
0.9	131.68	135.27	131.62
1.0	128.25	128.26	128.26

Table 9. Comparison of Experimental and Estimated Molecular Weights for Hexane (1) + Nonane (2) mixtures.

Mole fraction (1)	Molecular weight		
	Experimental	Kay's Rule	This study
0.0	128.25	128.26	128.26
0.2	116.53	119.84	117.35
0.4	119.75	111.43	123.19
0.6	101.28	103.01	100.74
0.8	96.68	94.60	95.05
1.0	86.22	86.18	86.18

Table 10. Comparison of Experimental and Estimated Molecular Weights for Hexane (1) + Toluene (2).

Mole fraction (1)	Molecular weight		
	Experimental	Kay's Rule	This study
0.0	92.15	92.14	92.14
0.2	87.75	90.95	89.06
0.4	96.25	89.76	99.23
0.6	82.41	88.56	86.61
0.8	88.11	87.37	87.79
1.0	86.22	86.18	86.18

Table 11. Comparison of Experimental and Estimated Molecular Weights for Toluene (1) + Tetradecane (2).

Mole fraction (1)	Molecular weight		
	Experimental	Kay's Rule	This study
0.0	198.49	198.40	198.40
0.2	171.48	177.15	173.46
0.4	173.95	155.90	172.36
0.6	129.79	134.64	131.67
0.8	113.12	113.39	113.94
1.0	92.15	92.14	92.14

hydrocarbon liquids (API ≥ 33) than Cragoe and Standing relations; the Isehunwa-Falade relation however proved best in such lighter hydrocarbons.

Table 12. AAD of different Correlations.

Correlations	Average Absolute Deviation (AAD)	
	15 – 32 API	33 - 55 API
Cragoe	1.53	1.35
Standing	0.12	0.95
Isehunwa-Falade	0.11	0.05
This Study	0.04	0.40

CONCLUSION

From the foregoing, it can be concluded that an improved empirical mixing rule based has been developed for determining the molecular weights of some binary mixtures. Similarly, an improved relation for predicting Molecular weight of petroleum oil and products from API gravity has been established.

NOMENCLATURE

AAD	Average absolute deviation
AGO	Automotive Gas Oil
AP	African Petroleum
DPK	Dual Purpose Kerosene
M	molecular weight
NNPC	Nigerian National Petroleum Corporation
NPDC	Nigerian Petroleum Development Company
P	pressure
T	temperature
y	mole fraction
P_b	bubble point, kg/cm^2
P_c	critical pressure, psia
T_b	normal boiling point temperature, R
T_c	critical temperature, R
M_a	apparent molecular weight of a gas mixture
M_i	molecular weight of the i^{th} component in the mixture
y_i	mole fraction of component i in the mixture
M	actual molecular weight measured
m	mass of solute in solvent
ΔFP	observed depression of freezing point (°C)
K_f	cryoscopic constant
ω	ancentric factor

Subscripts

b	boiling point
c	critical
i	property of component i

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