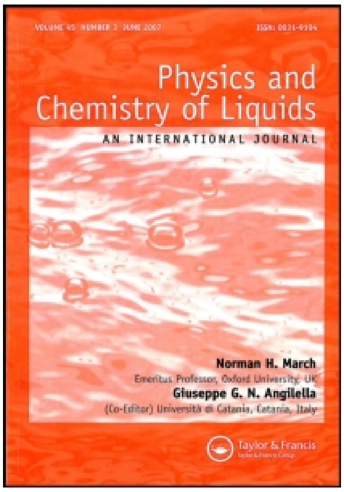

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Measurements and calculations of hydrocarbon mixtures liquid density by simple cubic equations of state

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The continuing importance of pressure-volume-temperature (PVT) property calculations of reservoir fluids mixtures in design of equipments used for storage, transportation and separation processes need considerable experimental and theoretical attempts to present a simple, accurate and theoretical based equation of state to replace the existing empirical based equations of state. The first author and his co-workers previously presented two parameters cubic theoretical based equation of state (MMM). This equation was used in PVT and vapour-liquid-equilibrium (VLE) calculations of pure and fluid mixtures. The comparisons for the different pure and mixture fluids calculations indicated the advantages of this equation of state over the well-known empirical-based two parameters cubic equation of state (RK EOS). In this study, PVT data for binary, ternary, quaternary and multicomponent oil mixtures at the different temperature and ambient pressure are measured, and reported. The measured PVT data were compared with those obtained by using the simple cubic equations of state. The calculated results by MMM EOS are compared with SRK and PR EOSs which are the commonly used three parameters cubic EOSs in the oil and gas calculations. The comparisons indicate that, although the SRK and PR EOSs needs an additional parameter (acentric factor, ω), the MMM equation of state is more accurate than both SRK and PR equations for the PVT calculations of oil mixtures.

Keywords: PVT equation of state; density; hydrocarbon mixtures; experimental measurements; petrochemical technology

1. Introduction

Thermodynamic characterisation of hydrocarbon mixtures has been an important research field in the chemical and petrochemical industries for many years [1]. In many cases, the pressure-volume-temperature (PVT) properties of pure and mixtures of hydrocarbons are required for design and operation steps of the different industrial processes, especially in oil and gas industries. PVT correlations or equations of states (EOSs) are frequently used to predict densities of liquid and gas hydrocarbon mixtures [2,3]. The simple cubic EOSs are widely used for calculations of PVT and VLE properties of multicomponent hydrocarbon mixtures [2,4]. Many comparative studies concerning accuracy of EOSs ability have been made to predict PVT properties of hydrocarbon mixtures [5,6]. The general conclusion is that the theoretical basis EOSs, makes them more suitable for extrapolation purposes, compared with the similar empirical equations [7,8].

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The thermodynamic properties of hydrocarbon mixtures that contain more heavy components would be difficult to predict from EOS than those of light hydrocarbons mixtures. The predictive capabilities of the EOSs for PVT properties can be checked by pure and mixture liquid density calculations [9].

Cubic equations of state may be classified into two categories: (1) Equations with two constant parameters like van der Waals and Redlich–Kwong (RK) [10] equations. They require two constant critical properties, such as critical temperature and pressure (T_c, P_c) for pure component calculations. (2) Those with more than two parameters and they include the Sove–Redlich–Kwong (SRK) [11] and Peng–Robinson (PR) [12] equations, which need another parameter such as acentric factor ω as well as T_c and P_c as the input parameters [7,8].

Pressure-volume-temperature (PVT) and vapour-liquid-equilibrium (VLE) properties for oil mixtures can be predicted through EOSs, once appropriate input data are provided for each equation [4,13,14]. The critical constants (T_c, P_c) for each component can be determined from experimental measurements or correlations [15,16]. There are several methods to calculate the acentric factor ω of hydrocarbon fractions using T_b, T_c and P_c as the input parameters [17–19].

A comparison between Lee–Kesler [17], Edmister [18] and Korsten [19] methods with actual values indicate that different methods for the prediction input parameters especially acentric factor give different values for heavy hydrocarbons. The reason for this variation is that different thermodynamic models predict different thermodynamic properties, for hydrocarbon mixtures containing heavy compounds [20].

The accuracy of available data and appropriate methods of estimation of basic input parameters for EOSs can vigorously effect on the accuracy of hydrocarbon mixture calculations. Therefore, for the minimum required input data, two parameters EOSs have considerable superiority to EOSs with more than two parameters for hydrocarbon mixtures calculations.

Among the first category of cubic EOSs, it is previously shown that the MMM EOS is generally superior to the RK EOS which was considered as the most accurate two parameters equation of state [2,7].

The objective of this study is to develop the PVT properties of hydrocarbon mixtures data, and the comparative studies of simple two (MMM) and three parameters (SRK and PR) cubic EOSs. Two cubic EOSs, SRK and PR EOSs, are considered in this article because they are frequently used for PVT and VLE calculations of hydrocarbon mixtures especially in oil and gas industries [21].

In this study, measured compositions and PVT properties of different binary, ternary and quaternary of five normal paraffin: n-C_5H_{12}, n-C_7H_{16}, n-C_8H_{18}, n-$C_{10}H_{22}$ and n-$C_{12}H_{26}$ and six multicomponent hydrocarbon mixtures obtained by distillation of the crude oil samples from the west and southwest of Iran were reported. The obtained PVT data were used to test the accuracy and validity of the MMM EOS against measured data and SRK and PR EOSs.

2. Experiment

Pure grade compounds, n-C_5H_{12}, n-C_7H_{16}, n-C_8H_{18}, n-$C_{10}H_{22}$ and n-$C_{12}H_{26}$ were obtained from Merck Co. Inc., Germany. All the samples were used without further purification.

Table 1. Operating condition for GC-mass analysis.

Column size	25 m × 0.53 mm
Column packing	5% diphenyl and 95% dimethylpolysiloxane
Detector type	FID
Detector temperature	523.15 K
Injector temperature	523.15 K
Oven temperature	$333.15\,\mathrm{K}\ (\mathrm{isotime} = 1\,\mathrm{min}) \xrightarrow{25K\,\mathrm{min}^{-1}} 545.15\,\mathrm{K}$
Carrier gas	Helium
Flow rate	$25\,\mathrm{cm}^3\,\mathrm{min}^{-1}$

Table 2. Comparison of measured liquid densities $\rho(\mathrm{g\,cm^{-3}})$, of pure compounds obtained from this work and literature [22].

Compounds	$\rho_{\mathrm{Exp.}}$	$\rho_{\mathrm{Lit.}}$
n-C_5H_{12}	0.6262	0.6257
n-C_7H_{16}	0.6837	0.6845
n-C_8H_{18}	0.7026	0.7026
n-C_9H_{20}	0.7220	0.7223

(*Continued*)

The binary, ternary and quaternary liquid mixtures were prepared by mass, using an analytical balance with ±0.1 mg accuracy (Shimadzu, model AEU 210). The oil mixtures were taken from six crude oil samples from the west and southwest of Iran. The crude oil samples were distillated in vacuum (600 mmHg) and the gas chromatography-mass spectrum (GC-mass) measurement was used to determine the composition of the distillated mixtures. The operating condition of GC-mass measurements is given in Table 1.

A 25 cm^3 calibrated glass pycnometer was used for density measurements at (295.15–311.15 K). The sample temperatures were regulated by using a thermostated constant temperature water bath. The temperature of water bath was measured to the accuracy of ±0.1 K by using a thermometer (Cole Parmer Instrument Company) with subdivisions of 0.1 K. To calibrate the glass pycnometer it was filled up with distilled water, and the weight of water was determined (accuracy ±0.1 mg). Using the reported accurate pure water densities [22] in the temperature range (295.15–311.15 K) the volume of pycnometer was determined with uncertainty $\pm 10^{-4}\,\mathrm{cm}^3$. For each solution, five density measurements were performed and the results were averaged. The uncertainty of density measurements was estimated as $\pm 10^{-4}\,\mathrm{g\,cm^{-3}}$.

3. Experimental results

Accuracy of the obtained PVT data was tested by comparison of the measured PVT properties of pure compounds with those obtained from literatures [22]. According to these comparisons, as reported in Table 2, the accuracy of the measured data is acceptable. The measured results for the binary mixtures of (n-C_7H_{16} + n-$C_{10}H_{22}$) at temperatures 295.15, 298.15, 303.15, 308.15 K are presented in Table 3. Table 4 shows the obtained PVT

Table 3. The measured density (g cm^{-3}) results for mixture of (n-C_7H_{16} + n-$C_{10}H_{22}$) at temperatures 295.15, 298.15, 303.15, 308.15 K.

	T (K)			
x_{C_7}	295.15	298.15	303.15	308.15
0.1004	0.7243	0.7199	0.7185	0.7131
0.2187	0.7206	0.7163	0.7143	0.7104
0.4114	0.7108	0.7053	0.7050	0.7006
0.6007	0.7040	0.6991	0.6977	0.6906
0.7999	0.6920	0.6891	0.6864	0.6804
1.0000	0.6827	0.6788	0.6733	0.6672

Table 4. The measured density (g cm^{-3}) results for mixture of (n-C_5H_{12} + n-$C_{12}H_{26}$) at temperatures 295.15, 298.15 K.

	T (K)	
x_{C_5}	295.15	298.15
0.7416	0.7416	0.7290
0.7314	0.7314	0.7265
0.7130	0.7130	0.6974
0.6948	0.6948	0.6946
0.6647	0.6647	0.6619
0.6200	0.6220	0.6164

Table 5. The measured density (g cm^{-3}) results for ternary mixture of (n-C_8H_{18} + n-C_7H_{16} + n-$C_{10}H_{22}$) at temperatures 295.15, 303.15, 311.15 K.

Mole fractions		T (K)		
x_{C_7}	x_{C_8}	295.15	303.15	311.15
0.451	0.0998	0.7094	0.7051	0.6984
0.4001	0.1993	0.7089	0.7031	0.6978
0.2996	0.3999	0.7055	0.7024	0.6964
0.1999	0.6005	0.7040	0.6994	0.6940
0.0999	0.7990	0.7016	0.6991	0.6936
0.0000	1.0000	0.7005	0.6963	0.6909

results of the binary mixtures of (n-C_5H_{12} + n-$C_{12}H_{26}$) at temperatures 295.15 and 298.15 K. The results of PVT measurements for the ternary mixture of (n-C_7H_{16} + n-C_8H_{18} + n-$C_{10}H_{22}$) at temperatures 295.15, 303.15, 311.15 K are reported in Table 5. The same results are shown in Table 6 for quaternary mixture of (n-C_7H_{16} + n-C_8H_{18} + n-$C_{10}H_{22}$ + n-$C_{12}H_{26}$) at temperatures 295.15, 303.15, 311.15 K. The obtained compositional analysis of the distillated crude oil samples are presented in Table 7. Table 8 shows the obtained PVT results of the distillated crude oil mixtures.

Table 6. The measured density ($g\,cm^{-3}$) results for quaternary mixture of (n-$C_8H_{18}+n$-$C_7H_{16}+n$-$C_{10}H_{22}+n$-$C_{12}H_{26}$) at temperatures 295.15, 303.15, 311.15 K.

Mole fractions			T (K)		
x_{C_7}	x_{C_8}	$x_{C_{10}}$	295.15	303.15	311.15
0.2296	0.0999	0.3001	0.7230	0.7200	0.7132
0.2664	0.1998	0.2675	0.7213	0.7175	0.7114
0.2002	0.4004	0.1996	0.7170	0.7131	0.7071
0.1332	0.5997	0.1338	0.7127	0.7078	0.7023
0.0665	0.7986	0.0683	0.7069	0.7030	0.6944
0.0000	1.0000	0.0000	0.7005	0.6963	0.6909

Tabel 7. Composition analysis of the distillated crude oil mixtures.

Components	Mole fractions mixture 1	Mole fractions mixture 2	Mole fractions mixture 3	Mole fractions mixture 4	Mole fractions mixture 5	Mole fractions mixture 6
n-Hexane						0.0643
Hexane, 2-methyl			0.1045			
Hexane, 3-methyl	0.0951	0.1069				
n-Heptane	0.0467	0.0812	0.0385	0.0357		0.0196
Pentane, 2,3-dimethyl					0.0892	
Cyclohexane, methyl	0.0559		0.0375	0.0297	0.0383	0.0340
Hexane, 2,4-demethyl			0.0283	0.0248	–	
Benzene, methyl	0.0768	0.1420	0.0716	0.0698	0.0803	0.0764
Heptane, 3-methyl	0.0505			0.0504		
Cyclohexane, 1,3-dimethyl			0.0683			
n-Octane	0.0699	0.0991	0.0873	0.0782	0.0709	0.0486
Heptane, 2,5-dimethyl	0.0293			0.0357		
Cyclohexane, ethyl			0.0388	0.0365		
Cyclohexane, 1,1,3-trimethyl		0.0355	0.036		0.0591	0.0414
Benzene, 1,3-dimethyl		0.1161	0.1176	0.0285	0.0994	0.1043
Benzene, 1,4-dimethyl	0.1245					
Benzene, 1,2-dimethyl	0.0242	0.0221	0.0228	0.1208		
n-Nonane	0.0853	0.0875	0.0826	0.0885	0.0611	0.0792
Octane, 2,6-dimethyl						0.0263
Octane, 3,6-dimethyl	0.0452				0.0414	
Nonane, 2-methyl	0.0275				0.0648	
Nonane, 3-methyl					0.0393	
Benzene,1,3,5-trimethyl			0.0291	0.0334	0.022	
Benzene,1,2,4-trimethyl	0.0884	0.0324	0.0309		0.0610	0.1080
n-Decane	0.0808	0.0815	0.0757	0.0874	0.0597	0.0561
Decan, 4-methyl						0.0495
n-Undecane	0.0672	0.0852	0.0761	0.1003	0.0672	0.0623
n-Dodecane	0.0327	0.0648		0.0785	0.0703	0.0617
n-Tridecane		0.0457	0.0543	0.0626	0.0366	0.0758
n-Tetradecane				0.0392	0.0395	0.0396
n-Pentadecane						0.0274
n-Hexadecane						0.0256

Table 8. The measured density ($g\,cm^{-3}$) results for the distillated oil mixtures at different temperatures.

	Mixture no.					
T (K)	1	2	3	4	5	6
288.65	0.7760	0.7836	0.7878	0.7965	0.8074	0.7794
293.15	0.7756	0.7830	0.7867	0.7954	0.8059	0.7774
298.15	0.7710	0.7792	0.7807	0.7922	0.8025	0.7733
303.15	0.7661	0.7731	0.7762	0.7854	0.7996	0.7693
308.15	0.7591	0.7682	0.7611	0.7814	0.7953	0.7513

Table 9. Comparison of the MMM, SRK and PR EOSs for density prediction of the studied binary, ternary and quaternary mixtures.

	AAD (%)		
Mixtures	MMM	SRK	PR
C_7+C_{10}	1.4	15.3	4.4
C_5+C_{12}	2.9	15.3	6.0
$C_7+C_8+C_{10}$	1.0	14.8	4.2
$C_7+C_8+C_{10}+C_{12}$	1.1	16.2	5.8

4. Calculations

4.1. *Binary, ternary and quaternary mixtures*

The densities of the binary, ternary and quaternary mixtures were calculated by using MMM, SRK and PR EOSs. Table 9 shows the comparisons of these results. According to this table, MMM equation of state is more accurate than SRK and PR equations for density calculations of presented mixtures.

4.2. *Distilled oil mixtures*

MMM equation of state has been used for PVT calculations of oil mixtures. The results are compared with those obtained by SRK and PR EOSs. The calculated results are shown in Table 10. For all calculations, k_{ij} are equal to zero. According to our comparisons, MMM equation of state has a better performance than SRK and PR equations for density calculations, however, application of MMM equation of state, does not need the acentric factor data.

5. Discussion

At present, the successful theories of statistical thermodynamics have been used for development of the theoretical equations of state. However, the simple cubic equations of state are still applied for chemical engineering calculations especially in oil and gas industries.

Table 10. Comparison of the MMM, SRK and PR EOSs for density prediction of the studied distillated crude oil mixtures.

Number of the distillated crude oil mixtures	AAD (%) MMM	SRK	PR
1	1.5	47.5	5.6
2	3.8	20.0	10.1
3	3.7	20.4	9.7
4	2.8	18.8	8.9
5	0.4	16.8	6.6
6	2.3	20.5	8.3

In this study, PVT properties of liquid binary, ternary, quaternary and multicomponent oil mixtures are measured at the different temperatures and ambient pressure, The obtained results were used for the comparative studies of the two parameter cubic MMM EOS with the three parameter SRK and PR EOSs, as the commoly used cubic EOSs. The comparisons indicate that the MMM EOS is better than SRK and PR equations for PVT calculations of the different liquid mixtures at the various temperatures. It is worth noting that, the SRK and PR EOSs needs an additional parameter (acentric factor, ω) respect to MMM EOS.

The acceptable performance of MMM EOS indicate that the theoretical basis EOSs can be successfully used for pure fluid and mixture of fluids, especially for oil mixture calculations with the minimum required input parameters. By considering the lack of accurate characterisation data of pure heavy hydrocarbons such as T_c, P_c and ω which may be used as the EOSs input parameters, the two parameters EOSs have a valuable superority to those with more than two parameters for oil mixture calculations.

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