

Scientific paper

Isomorphic Viscosity Equation of State for Binary Fluid Mixtures

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Abstract

The thermodynamic behavior of the simple binary mixtures in the vicinity of critical line has a universal character and can be mapped from pure components using the isomorphism hypothesis. Consequently, based upon the principle of isomorphism, critical phenomena and similarity between $P - \rho - T$ and $T - \eta - (\text{viscosity}) - P$ relationships, the viscosity model has been developed adopting two cubic, Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR), equations of state (EoS) for predicting the viscosity of the binary mixtures. This procedure has been applied to the methane-butane mixture and predicted its viscosity data. Reasonable agreement with the experimental data has been observed. In conclusion, we have shown that the isomorphism principle in conjunction with the mapped viscosity EoS suggests a reliable model for calculating the viscosity of mixture of hydrocarbons over a wide pressure range up to 35 MPa within the stated experimental errors.

Keywords: Viscosity, Critical Phenomena, Isomorphism Principle and Binary Mixture.

1. Introduction

Accurate prediction of the critical properties and evaluation of the phase behavior of pure substances and mixtures are the basis for developing and improving EoS. The primary and simplest extension on the construction of EoS is done starting from van der Waals (vdW), Berthelot, and Dieterici EoS.¹ Nevertheless, the classical EoS do not predict universality of the critical point, so subsequent studies attempted to achieve this universality.^{2,3}

Due to the presence of large fluctuations near the critical point, some singular phenomena including the critical opalescence can occur.⁴ The first non-classical model with effective critical exponents for describing the phase behavior of the binary mixtures was developed by Leung and Griffiths⁵ and subsequently modified by Moldover, Rainwater and their *co-workers*^{6–8} to obtain a satisfactory prediction of the thermo-physical properties for many binary mixtures. Thereafter, for fluid mixtures a scaled EoS was proposed for analyzing the asymmetric fluid-phase behavior asymptotically close to the critical point using the principle of isomorphism.^{9,10} When two structures are

the same but have different labels (for example liquid-solid and vapor-liquid phase diagram), we say that the structures are isomorphism. There are some elements in thermodynamics which are isomorphic to elements in the calculus. For example, Definitions of H, A, and G of thermodynamics are isomorphic to Legendre transforms in the calculus. Our important role in thermodynamic is to find the specific isomorphic elements in the calculus in order to account for all asymmetric features of critical phase transitions in fluids. If one want to extend a model to describe a new phase transition, a more general scaling field and convenient elements in the calculus is required. This approach was developed through relating the two relevant scaling fields to the linear combinations of three physical field variables – the temperature, pressure and chemical potentials of the two components.^{11–16}

Moreover, based on an asymmetric EoS, the crossover equation of state was considered to extend its range of applicability to a wider region around the critical point for the single and two-component fluids.^{17–21}

In the vicinity of critical point, the viscosity of fluid is one of the thermo-physical properties which exhibits an increasing anomaly.²² Such critical abnormal behaviors

were considered theoretically and experimentally.²³ Recognizing the similarity between $P - \rho - T$ and $T - \eta - P$ relationships,²⁴ many researches attempted to develop EoS-based viscosity models using cubic EoS including vdW, Patel-Teja and PR.^{25,26} Developing a viscosity model based on an EoS has some advantages such as describing the viscosity of both gas and liquid phases by a single model, correlating both high and low pressure data and evaluating the fluid viscosity without including the density. As a result, the P - V - T , V - L - E and fluid viscosity can be calculated using a single EoS²⁵ via the isomorphism principle.

In this work, using the critical isomorphism principle, the thermodynamical free energy of two SRK and PR EoS was derived for binary fluid mixtures. The reason for choosing classical SRK and PR EoS was the capability the former for fitting the experimental data and predicting the phase behavior of mixtures in the critical regions and that of the latter for accurately predicting the vapor-liquid equilibrium of the pure substances and equilibrium ratios of the components in the mixtures. Thus, based on the similarity between $P - \rho - T$ and $T - \eta - P$ relationships, the viscosity model for binary mixture has been derived.

We proceed as follows. In Sec. 2 by using the classical SRK and PR EoS, the viscosity model has been derived based on one-component fluids EoS. In Sec.3 we describe the specific procedure adopted for mapping the thermodynamic surface of the mixtures to that of one-component fluids following the ideas of Griffiths and Wheeler²⁷ and Leung and Griffiths⁵ and then formulate a corresponding isomorphous Helmholtz free energy for prediction the viscosity of fluid mixtures. In Sec.4 comparison is made with the experimental viscosity data for mixtures of methane-butane. Concluding remarks are presented in Sec. 5.

2. Viscosity Model Based on Cubic EoS

The pressure form of SRK EoS is:

$$P = \frac{RT\rho}{1-b\rho} - \frac{a(T)\rho^2}{1+b\rho}, \quad (1)$$

where P , ρ , T and R are pressure, molar density, temperature and gas constant, respectively.

The coefficients a and b are given by:

$$a(T) = \frac{0.4274[1+k(1-T_r^{0.5})]^2 R^2 T_c^2}{P_c}, \quad (2)$$

$$b = \frac{0.08664 RT_c}{P_c}, \quad (3)$$

with

$$k = 0.48 + 1.571\omega - 0.176\omega^2, \quad (4)$$

in which $T_r = T/T_c$ is reduced temperature, ω is the acentric factor and T_c and P_c are the critical temperature and pressure, respectively.

According to the similarity between $P - \rho - T$ and $T - \eta - P$ relationships, in the SRK EoS, ρ and η are interchanged and T and gas constant R are replaced by P and r , respectively. Then Eq. (1) is changed to the following SRK viscosity equation:

$$T = \frac{rP\eta}{1-b'\eta} - \frac{a\eta^2}{1+b\eta}. \quad (5)$$

Similar to $(\partial P/\partial \rho)_T = 0$ and $(\partial^2 P/\partial \rho^2)_T = 0$, on the critical isobar at the critical point of the $T - \eta - P$ diagram, we have:

$$(\partial T/\partial \eta)_P = 0, \quad (6)$$

$$(\partial^2 T/\partial \eta^2)_P = 0, \quad (7)$$

$$\frac{T_c}{P_c r_c \eta_c} = Z_c. \quad (8)$$

The structure of the critical viscosity equation can be estimated with the following equation:

$$\eta_c = 7.7 T_c^{-1/6} M^{1/2} P_c^{2/3}, \quad (9)$$

in which M is molecular weight.

By applying the constraints of Eqs. (6) and (7) to the Eq. (5), we can write:

$$a = \frac{0.4274 r_c^2 P_c^2}{T_c}, \quad (10)$$

$$b = \frac{0.08664 r_c P_c}{T_c}. \quad (11)$$

Parameters r and b' in Eq. (5) are both functions of P_r and T_r as:²⁵

$$r = r_c \tau(T_r, P_r), \quad (12)$$

$$b' = b \varphi(T_r, P_r), \quad (13)$$

and the functional form of $\tau(T_r, P_r)$ and $\varphi(T_r, P_r)$ were adopted as follow:²⁵

$$\tau(T_r, P_r) = \{1 + Q_1 [(P_r T_r)^{0.5} - 1]\}^{-2}, \quad (14)$$

$$\varphi(T_r, P_r) = \exp[Q_2 (\sqrt{T_r} - 1) + Q_3 (\sqrt{P_r} - 1)], \quad (15)$$

in which Q_i were generalized in terms of acentric factor ω and molecular weight M in the following forms:²⁵

$$Q_1 = 0.79875 + 2.57404 \omega + 0.006232 M + 0.065526 \omega M - 13.165058 \omega^2 - 0.000079 M^2, \quad (16)$$

$$Q_2 = 1.138605 - 31.783684 \omega + 0.088274 M + 0.242397 \omega M + 76.541489 \omega^2 - 0.001617 M^2, \quad (17)$$

$$Q_3 = 0.350433 + 3.017745 \omega - 0.006269 M + 0.207998 \omega M - 31.620953 \omega^2 - 0.00037 M^2. \quad (18)$$

Thermodynamic properties were made dimensionless using the critical parameters:

$$\begin{aligned} \tilde{P} &= \frac{P}{P_c}, & \tilde{\eta} &= \frac{\eta}{\eta_c}, & \tilde{T} &= \frac{T}{T_c} \frac{P_c}{P}, \\ \tilde{\mu} &= \frac{\mu}{P} \frac{P_c \eta_c}{T_c}, & \tilde{A} &= \frac{\eta A P_c}{P T_c}. \end{aligned} \quad (19)$$

In addition, defining:

$$\Delta \tilde{P} = 1 + \tilde{P}, \quad \Delta \tilde{\eta} = \tilde{\eta} - 1. \quad (20)$$

the SRK viscosity equation can be re-expressed in terms of dimensionless variables:

$$\tilde{T} = \frac{1}{Z_c} \left[\frac{r \tilde{\eta}}{(1 - Z_1 \tilde{\eta} \phi)} + \frac{Z_2 \tilde{P} \tilde{\eta}^2}{(1 + Z_1 \tilde{\eta})} \right], \quad (21)$$

where

$$Z_1 = \frac{0.08664}{Z_c}, \quad (22)$$

$$Z_2 = \frac{0.4274}{Z_c}. \quad (23)$$

Analogous to $(\partial \tilde{\mu} / \partial \tilde{P})_T = \tilde{P}^{-1} (\partial \tilde{P} / \partial \tilde{P})_T$, we have $(\partial \tilde{\mu} / \partial \tilde{\eta})_T = \tilde{\eta}^{-1} (\partial \tilde{T} / \partial \tilde{\eta})_T$. Thus, Eq. (21) can be integrated to yield:

$$\tilde{\mu} = \int \tilde{\eta}^{-1} (\partial \tilde{T} / \partial \tilde{\eta})_T d\tilde{\eta}, \quad (24)$$

Using the thermodynamic relation:

$$\tilde{A} = \tilde{\eta} \tilde{\mu} - \tilde{T}, \quad (25)$$

the corresponding equation for the dimensionless Helmholtz free energy of the viscosity can be obtained as:

$$\begin{aligned} \tilde{A} &= \frac{4.9331 \tilde{\eta} \tilde{P}}{Z_c} + \frac{4.9331 \tilde{\eta} \tilde{P} \ln[1 + Z_1 \tilde{\eta}]}{Z_c} + \frac{6.9875 \tilde{\eta} \ln[\tilde{\eta} \phi[T_r, P_r]] \tau[T_r, P_r]}{Z_c} \\ &\quad - \frac{\tilde{\eta} \tau[T_r, P_r] \ln[1 - Z_1 \tilde{\eta} \phi[T_r, P_r]]}{Z_c} + \frac{\tilde{\eta} \tau[T_r, P_r]}{1 - Z_1 \tilde{\eta} \phi[T_r, P_r]} \left(1 - \frac{1}{Z_c} \right) + \tilde{\eta} \mu^0[\Delta \tilde{P}], \end{aligned} \quad (26)$$

where $\mu^0[\Delta \tilde{P}]$ is a pressure-dependent integration constant.

Similarly, viscosity equation based on PR EoS can be formulated as:

$$T = \frac{rP\eta}{1 - b'\eta} - \frac{a\eta^2}{1 + b\eta + b\eta(1 - b\eta)}, \quad (27)$$

$$a = \frac{0.45724 r_c^2 P_c^2}{T_c}, \quad (28)$$

$$b = \frac{0.07780 r_c P_c}{T_c}, \quad (29)$$

$$\begin{aligned} \tilde{A} &= \frac{\tilde{\eta} \tau[T_r, P_r]}{Z_c} \ln \left(\frac{\tilde{\eta}}{1 - Z_1 \tilde{\eta} \phi[T_r, P_r]} \right) - \\ &\quad - \frac{12.4673 \tilde{\eta} \tilde{P}}{Z_c} \operatorname{arctanh}(0.70711(1 + Z_1 \tilde{\eta})) + \\ &\quad + \tilde{\eta} \mu^0[\Delta \tilde{P}], \end{aligned} \quad (30)$$

$$Z_1 = \frac{0.07780}{Z_c}, \quad (31)$$

$$Z_2 = \frac{0.45724}{Z_c}, \quad (32)$$

where definitions of r , b' , $\tau(T_r, P_r)$ and $\phi(T_r, P_r)$ are analogous to Eqs. (12)–(15).

3. The Isomorphism Principle of Critical Phenomena

The principle of critical isomorphism can project the critical behavior of fluids and fluid mixtures onto that of the Ising model such that one can use the appropriate isomorphic thermodynamic quantities.^{16,27,29,30} The thermodynamic properties for binary mixtures can be defined as:

$$\begin{aligned} \hat{T} &= \frac{1}{RT}, & \hat{P} &= \frac{P}{RT}, & \hat{\mu}_1 &= \frac{\mu_1}{RT}, \\ \hat{\mu}_2 &= \frac{\mu_2}{RT}, & \hat{A} &= \frac{\rho A}{RT}, & \hat{U} &= \rho U. \end{aligned} \quad (33)$$

where $\hat{\mu}_1$ and $\hat{\mu}_2$ are the chemical potentials of the two components, respectively.

According to the viscosity model, thermodynamic properties can be given as:

$$\begin{aligned} \hat{T} &= \frac{T}{r_c P}, & \hat{P} &= \frac{1}{r_c P}, & \hat{\mu}_1 &= \frac{\mu_1}{r_c P}, \\ \hat{\mu}_2 &= \frac{\mu_2}{r_c P}, & \hat{A} &= \frac{\eta A}{r_c P}, & \hat{U} &= \eta U. \end{aligned} \quad (34)$$

Also, the modified isomorphous Helmholtz free energy density of viscosity \hat{A} can be written as:³¹

$$\hat{A}_{\text{iso}}(\hat{P}, \eta, \zeta) = \eta h - \hat{T}, \quad (35)$$

here, h (the ordering field) and ζ (the isomorphous field variable which is often called the hidden field) are related to the activities satisfying the following differential equation:

$$d\hat{A}_{\text{iso}} = \hat{U}d\hat{P} + h d\eta - w d\zeta, \quad (36)$$

where $w = \frac{\eta(x-\zeta)}{\zeta(1-\zeta)}$ is the density variable which is conjugated to the ζ . The critical parameters T_c , P_c and η_c will diverge along this line of critical points as functions of the mole fraction x or of a hidden field ζ . The mole fraction x of the component 2 with larger molecular volume is interrelated to ζ by using Eq. 36 and the definition of w through:³¹

$$x = \zeta - \frac{\zeta(1-\zeta)}{\eta} \left(\frac{\partial \hat{A}_{\text{iso}}}{\partial \zeta} \right)_{\hat{P}, \eta}. \quad (37)$$

Implementing the isomorphism principle, the deviation variables can be considered as a function of ζ :

$$\Delta \tilde{P} = \frac{P - P_c(\zeta)}{P}, \quad \Delta \tilde{\eta} = \frac{\eta - \eta_c(\zeta)}{\eta_c(\zeta)}. \quad (38)$$

The isomorphism principle states that for a mixture at constant ζ , the $\hat{A}_{\text{iso}}(\hat{P}, \eta, \zeta)$ will be the same singular function of $\Delta \tilde{P}$ and $\Delta \tilde{\eta}$ as the Helmholtz free-energy of a one-component fluid,¹⁹ while all system-dependent constants will depend on the hidden field, parametrically.²⁰ Subsequently, in the one-component limit $\hat{A}_{\text{iso}} \rightarrow \hat{A} = (T/r_c P)\bar{A}$ and we can write:

$$\hat{A}_{\text{iso}}(\hat{P}, \eta, \zeta) = \frac{T_c(\zeta)}{r_c(\zeta) P_c(\zeta)} \tilde{A}(\Delta \tilde{P}, \Delta \tilde{\eta}, \zeta), \quad (39)$$

where $\tilde{A}(\Delta \tilde{P}, \Delta \tilde{\eta}, \zeta)$ is given by the chosen classical EoS. By replacing Eq. (26) in Eq. (39) and using the relation:

$$\hat{T} = \eta \left(\frac{\partial \hat{A}_{\text{iso}}}{\partial v} \right)_{\Delta \tilde{P}, \zeta} - \hat{A}_{\text{iso}}, \quad (40)$$

the isomorphous viscosity EoS becomes:

$$\tilde{T} = \frac{T_c(\zeta) P}{P_c(\zeta)} \left[\eta \left(\frac{\partial \tilde{A}}{\partial \eta} \right)_{\Delta \tilde{P}, \zeta} - \tilde{A} \right]. \quad (41)$$

Since the critical parameters $T_c(\zeta)$, $\eta_c(\zeta)$, and $P_c(\zeta)$ are functions of the field variable ζ while the experimental data for these parameters are available only as functions of the mole fraction x , in order to apply the isomorphous viscosity EoS to the mixtures, the variable x have to be converted into the variable ζ by using Eq. (41). Nevertheless, for this determination we need \hat{A}_{iso} , which depends on $T_c(\zeta)$, $v_c(\zeta)$, and $P_c(\zeta)$. This procedure can be simplified if the field variable ζ is selected at the critical line condition (CLC). In this way, it numerically becomes equal to the mole fraction x .

In principle, there are a number of different methods in which one can implement the CLC as an expressed function of the critical parameters.^{20,31,32} In this paper, we adopt the following relationship between the mole fraction x and the field variable ζ as:

$$\begin{aligned} x = \zeta - \frac{\zeta(1-\zeta)}{v} \Delta \tilde{P} & \left[\frac{1}{P_c(\zeta)} \frac{dP_c}{d\zeta} \frac{T_c(x)}{r_c(x) P_c(x)} + \right. \\ & + \frac{1}{r_c(x)} \frac{d(T_c/P_c)}{d\zeta} - \frac{v}{v_c^2(\zeta)} \frac{dv_c}{d\zeta} \frac{T_c(x)}{r_c(x) P_c(x)} \\ & \left. + 7.7 \frac{T_c(x)}{r_c(x) P_c(x)} \right]. \end{aligned} \quad (42)$$

4. Applications

In this work, we are attempting to apply SRK and PR viscosity equation such that the isomorphous Helmholtz free-energy can represent the experimental viscosity data for methane + butane mixture. For this purpose, the system-dependent parameters for the pure fluids were represented in Table 1 to determine the EoS.

The critical temperature $T_c(\zeta)$, critical density $\rho_c(\zeta)$, and critical pressure $P_c(\zeta)$ should be specified as functions of the hidden field ζ to determine the isomorphous equation \hat{A}_{iso} for the mixture. Since along the critical line $\zeta = x$, the quantities $T_c(\zeta)$, $\rho_c(\zeta)$, and $P_c(\zeta)$ can be defined as:

$$T_c(\zeta) = T_c(x), \quad \rho_c(\zeta) = \rho_c(x), \quad (43)$$

Table 1. System-dependent critical parameters for methane and butane pure fluids.^{33–35}

System-dependent parameters	Methane	Butane
T_c (K)	190.564	425.20
ρ (kg/m ³)	162.66	227.85
P_c (MPa)	4.5992	3.796
M (g/mol)	16.0428	58.125
ω	0.008	0.193

In practice, the critical temperature and pressure are characterized by a polynomial form as:²⁰

$$T_c(x) = T_c^{(1)}(1-x) + T_c^{(2)}x + (T_1 + T_2x + T_3x^2 + T_4x^3 + T_5x^4)x(1-x), \quad (44)$$

$$P_c(x) = P_c^{(1)}(1-x) + P_c^{(2)}x + (P_1 + P_2x + P_3x^2 + P_4x^3 + P_5x^4)x(1-x), \quad (45)$$

where x is the mole fraction of the component 2 and $T_c^{(i)}$ and $P_c^{(i)}$ (with $i = 1, 2$) are the critical parameters of the corresponding components.

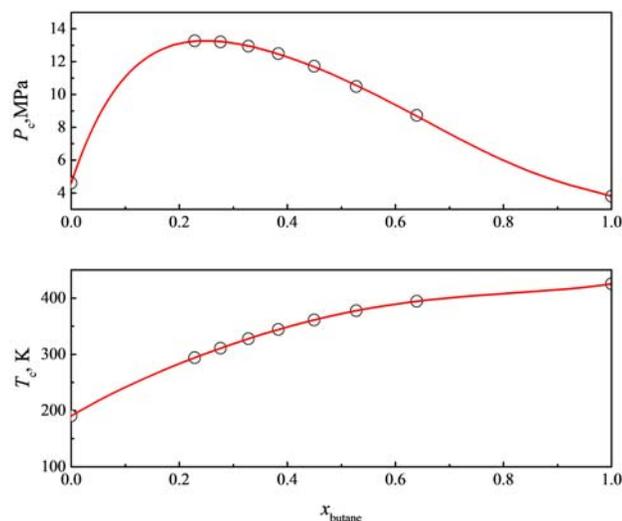


Fig. 1 $T_c(x)$ and $P_c(x)$ for methane + butane mixture as a function of butane Mole fraction, x_{butane} . The curves represent the values calculated using Eqs. (40)–(41), the symbols indicate experimental data obtained by Sage *et al.*³⁶

Thus, the values of the coefficients T_i and P_i ($i = 1-5$) are determined from fitting to the experimental data using Eqs. (44)–(45). The results for the fitting parameters were given in Table 2. Comparison of the calculated values from Eqs. (44)–(45) with the experimental data reported by Sage *et al.*³⁶ were shown in Fig. 1.

Table 2. Critical-Line Parameters (CLP) of the methane + butane mixture.

T_i (K)	P_i (MPa)
$T_1 = 337.4213$	$P_1 = 96.2223$
$T_2 = -438.701$	$P_2 = -298.7019$
$T_3 = 1175.242$	$P_3 = 532.9796$
$T_4 = -1505.42$	$P_4 = -539.1141$
$T_5 = 530.8798$	$P_5 = 227.8896$

Using Eq. (9) for $\eta_c(\zeta)$, we have:

$$\eta_c(\zeta) = 7.7T_c(\zeta)^{-1/6} M(\zeta)^{1/2} P_c(\zeta)^{2/3}, \quad (46)$$

with

$$M(\zeta) = M_1(1-\zeta) + M_2\zeta, \quad (47)$$

where M_1 and M_2 are molecular weights of the corresponding components.

By adopting SRK and PR EsoS one at a time, $Z_c(\zeta)$ becomes:

$$Z_c(\zeta) = Z_c^{cl} = 0.333, \quad (48)$$

and

$$Z_c(\zeta) = Z_c^{cl} = 0.307, \quad (49)$$

respectively. The isomorphic EoS also contains the system-dependent Constants, $Q_i(\zeta)$ ($i = 1-3$), as a function of the variable ζ . Therefore, a quadratic interpolation formula (Eq. (50)) has been adopted to determine $Q_i(\zeta)$ as:

$$Q_i(\zeta) = Q_i^{(1)}(1-\zeta) + Q_i^{(2)}\zeta + Q_i^{(12)}\zeta(1-\zeta), \quad (50)$$

where $Q_i^{(1)}$ and $Q_i^{(2)}$ are the system-dependent coefficients of methane and ethane, respectively and $Q_i^{(12)}$ are mixing coefficients which are determined by fitting the available viscosity data for the mixtures. All these system-dependent coefficients were reported in Table 3.

Table 3. System-dependent constants of methane + butane mixture for the two viscosity EsoS.

	SRK EoS	PR EoS
$Q_1^{(12)}$	-7.55	-8.19
$Q_2^{(12)}$	2.25	2.55
$Q_3^{(12)}$	-3.00	-1.75

A comparison between the calculated η from the isomorphic SRK and PR viscosity equation with those of the experimental data reported by Carmichael *et al.*³⁷ were shown in Fig. 2–3.

Also, predicting the two viscosity EsoS, the average absolute deviation of the viscosity at $x = 0.394$ for the three isothermal mixture of methane + butane in the considered pressure range were given in Table 4. Clearly, the isomorphic viscosity equations yield an acceptable representation for the viscosity data. On the other hand, one can optimize and determine the coefficients in eq. (16)–(18) for each EoS to establish a better fitting of the data to obtain the posted accuracy at low temperature and pressure. Here, we wanted to use the principle of the corresponding states for calculating these EsoS parameters. Furthermore, Harstad *et al.*³⁸ indicated that the Peng-Robinson EoS could be used to obtain a relatively accurate and computationally efficient correlation of fluid mixtures at high-pressure.

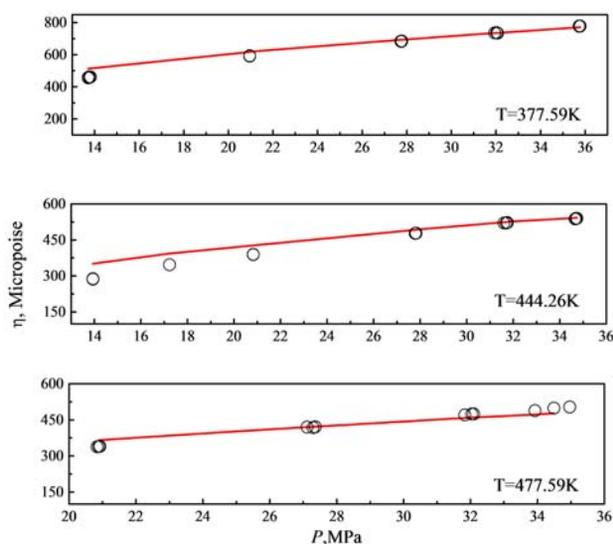


Fig. 2. Comparison between the calculated and experimental isothermal $\eta - P$ curves for a methane + butane mixture in $x = 0.394$ mole fraction of butane. The curves represent the values calculated using the isomorphic SRK viscosity equation, symbols indicate values obtained by Carmichael *et al.*³⁷

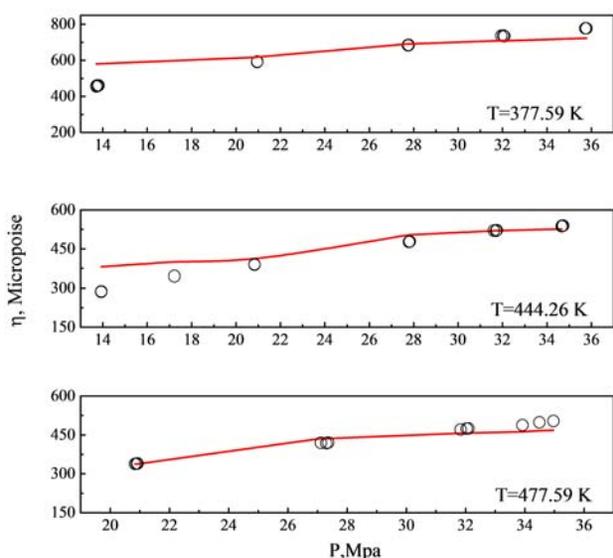


Fig. 3. Comparison between the calculated and experimental isothermal $\eta - P$ curves for a methane + butane mixture in $x = 0.394$ mole fraction of butane. The curves represent the values calculated using isomorphic PR viscosity equation, symbols indicate values obtained by Carmichael *et al.*³⁷

Table 4. Average absolute deviation of viscosity prediction obtained by the two viscosity EoS for the three isothermal mixture of methane + butane at $x = 0.394$ in the considered pressure range.

Temperature	AAD (%) SRK EoS	AAD (%) PR EoS	Pressure range (MPa)
$T = 377.59\text{K}$	1.41	3.98	20.95~35.78
$T = 444.26\text{K}$	2.98	2.78	20.83~34.73
$T = 477.59\text{K}$	3.83	3.50	20.83~34.97

5. Conclusions

The thermodynamic behavior of the simple binary mixtures including the critical region has a universal character and can be described by a single one-component fluid model using the isomorphism hypothesis. In this paper, we have shown that in terms of SRK and PR EoS, how this principle can be applied using the similarity between $P - \rho - T$ and $P - \eta - P$ relationships and as a result, the viscosity model may be developed for predicting the viscosity of binary mixtures. Moreover, the EoS-based viscosity models have been successfully extended to the binary mixtures and accordingly, an extended relationship between the concentration x and the hidden field ζ has been introduced. Therefore, the isomorphic SRK and PR viscosity equations yield a satisfactory representation for the hydrocarbon mixtures by applying conventional mixing rules for the mixing parameters. The close agreement between the predicted values and the experimental results of the viscosity in a wide pressure range (about 20.8–35.8 MPa) demonstrate the utility of the isomorphism principle.

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7. References

- J. J. Martin, Y. C. Hou, *AIChE J.* **1955**, *1*(2), 142–151. <http://dx.doi.org/10.1002/aic.690010203>
- M. E. Fisher, *Rev. Mo. Phys.* **1974**, *46*(4), 597–616. <http://dx.doi.org/10.1103/RevModPhys.46.597>
- K. G. Wilson, *Phys. Rev. B* **1971**, *4*(9), 3174–3183. <http://dx.doi.org/10.1103/PhysRevB.4.3174>
- J. M. H. Levelt Sengers, Effects of critical fluctuations on the thermodynamic and transport properties of supercritical fluids, in: E. Kiran and J. M. H. Levelt Sengers (Eds.), *Supercritical Fluids, Fundamentals for Application*, NATO ASI Ser. E, 273, Kluwer, Dordrecht, **1994**, pp. 231–272.
- S. S. Leung, R. B. Griffiths, *Phys. Rev. A* **1973**, *8*(5), 2670–2683. <http://dx.doi.org/10.1103/PhysRevA.8.2670>
- M. R. Moldover, J. S. Gallagher, *AIChE J.* **1978**, *24*(2), 267–278. <http://dx.doi.org/10.1002/aic.690240216>
- M. R. Moldover, J. C. Rainwater, *J. Chem. Phys.* **1988**, *88*(12), 7772–7780. <http://dx.doi.org/10.1063/1.454290>
- J. C. Rainwater, in: Ely, J. F., Bruno, T.J. (Eds.), *Supercritical Fluid Technology*, CRC, Boca Raton, FL, p. 57.
- M. A. Anisimov, S. B. Kiselev, S. E. Khalidov, *Int. J. Thermophys.* **1988**, *9*(3), 453–464. <http://dx.doi.org/10.1007/BF00513083>

10. M. A. Anisimov, S. B. Kiselev, I. G. Kostukova, *J. Heat Transfer* **1988**, 110(4a), 986–991.
<http://dx.doi.org/10.1115/1.3250603>
11. A. Jamali, H. Behnejad, *Phys. Chem. Liquids* **2013**, 52(4), 519–532. <http://dx.doi.org/10.1080/00319104.2013.842471>
12. A. Jamali, H. Behnejad, K. Hosseini, *J. Mol. Liquids* **2014**, 197, 93–99. <http://dx.doi.org/10.1016/j.molliq.2014.04.031>
13. Y. C. Kim, M. E. Fisher, G. Orkoulas, *Phys. Rev. E* **2003**, 67(6), 061506.
<http://dx.doi.org/10.1103/PhysRevE.67.061506>
14. P. Losada-Pérez, C. Glorieux, J. Thoen, *J. Chem. Phys.* **2012**, 136, 144502. <http://dx.doi.org/10.1063/1.3701286>
15. G. Pérez-Sánchez, P. Losada-Pérez, C. A. Cerdeiriña, J. V. Sengers, M. A. Anisimov, *J. Chem. Phys.* **2010**, 132, 154502. <http://dx.doi.org/10.1063/1.3378626>
16. J. Wang, C. A. Cerdeiriña, M. A. Anisimov, J. V. Sengers, *Phys. Rev. E* **2008**, 77(3), 031127.
<http://dx.doi.org/10.1103/PhysRevE.77.031127>
17. A. Bakhshandeh, H. Behnejad, *Chem. Phys.* **2012**, 409, 32–36. <http://dx.doi.org/10.1016/j.chemphys.2012.09.024>
18. A. Bakhshandeh, H. Behnejad, *J. Iran. Chem. Soc.* **2013**, 10(2), 367–377.
19. Z. Y. Chen, A. Abbaci, S. Tang, J. V. Sengers, *Phys. Rev. A* **1990**, 42(8), 4470–4484.
<http://dx.doi.org/10.1103/PhysRevA.42.4470>
20. G. X. Jin, S. Tang, J. V. Sengers, *Phys. Rev. E* **1993**, 47(1), 388–402. <http://dx.doi.org/10.1103/PhysRevE.47.388>
21. S. B. Kiselev, I. G. Kostyukova, A. A. Povodyrev, *Int. J. Thermophys* **1991**, 12(5), 877–895.
<http://dx.doi.org/10.1007/BF00502413>
22. J. T. R. Watson, R. S. Basu, J. V. Sengers, *J. Phys. Chem. Ref. Data* **1980**, 9(4), 1255–1290.
<http://dx.doi.org/10.1063/1.555631>
23. Y. Arai, T. Sako, Y. Takebayashi, *Supercritical Fluids: Molecular Interactions, Physical Properties, and New Applications*. Editor, Springer Berlin Heidelberg, **2002**.
24. P. Phillips, *Proc. R. Soc. London. Series A* **1912**, 87(592), 48–61.
25. X. Q. Guo, L. S. Wang, S. X. Rong, T. M. Guo, *Fluid Phase Equilib.* **1997**, 139(1–2), 405–421.
[http://dx.doi.org/10.1016/S0378-3812\(97\)00156-8](http://dx.doi.org/10.1016/S0378-3812(97)00156-8)
26. J. E. Little, H. T. Kennedy, *Soc. Pet. Eng.* **1968**, 6, 157–162.
27. R. B. Griffiths, J. C. Wheeler, *Phys. Rev. A* **1970**, 2, 1047–1064. <http://dx.doi.org/10.1103/PhysRevA.2.1047>
28. O. A. Uyehara, K. M. Watson, *Natl. Petroleum News* **1944**, 36, R–714.
29. H. Behnejad, J. V. Sengers, M. A. Anisimov, Thermodynamic Behaviour of Fluids near Critical Points, in: A. R. H. Goodwin, J. V. Sengers, C. J. Peters (Eds.), *Applied Thermodynamics of Fluids*. The Royal Society of Chemistry, Cambridge, **2010**, PP. 321–367..
30. W. F. Saam, *Phys. Rev. A* **1970**, 2(4), 1461–1466.
<http://dx.doi.org/10.1103/PhysRevA.2.1461>
31. K. S. Abdulkadirova, C. J. Peters, J. V. Sengers, M. A. Anisimov, *J. Supercritical Fluids* **2010**, 55(2), 594–602.
32. S. B. Kiselev, A. A. Povodyrev, *Fluid Phase Equilib.* **1992**, 79, 33–47.
[http://dx.doi.org/10.1016/0378-3812\(92\)85118-R](http://dx.doi.org/10.1016/0378-3812(92)85118-R)
33. R. H. Sage, B. L. Hicks, W. N. Lacey, *Ind. Eng. Chem.* **1940**, 32(8), 1085–1092.
<http://dx.doi.org/10.1021/ie50368a014>
34. U. Setzmann, W. Wagner, *J. Phys. Chem. Ref. Data* **1991**, 20(6), 1061–1155. <http://dx.doi.org/10.1063/1.555898>
35. B. A. Younglove, J. F. Ely, *J. Phys. Chem. Ref. Data* **1987**, 16(4), 577–798. <http://dx.doi.org/10.1063/1.555785>
36. R. H. Sage, B. L. Hicks, W. N. Lacey, *Ind. Eng. Chem.* **1940**, 32(8), 1085–1092. <http://dx.doi.org/10.1021/ie50368a014>
37. L. T. Carmichael, V. M. Berry, B. H. Sage, *J. Chem. Eng. Data* **1967**, 12(1), 44–47.
<http://dx.doi.org/10.1021/je60032a014>
38. K. G. Harstad, R. S. Miller, J. Bellan, *AIChE J.* **1997**, 4
<http://dx.doi.org/10.1002/aic.690430624>

Povzetek

Termodinamske lastnosti enostavnih binarnih mešanic v bližini kritične točke so univerzalne in jih lahko napovemo s pomočjo hipoteze o izomorfizmu. V tem delu smo z uporabo Soave-Redlich-Kwongove in Peng-Robinsonove enačbe stanja za napoved vrednosti viskoznosti binarnih mešanic razvili model za opis relacij $P - \rho - T$ in $T - \eta - (\text{viskoznost}) - P$. Postopek smo preverili z eksperimentalnimi podatki za mešanice metana in butana in opazili primerno ujemanje. Tako smo pokazali, da načelo izomorfizma z uporabo navedenih enačb stanja predstavlja zanesljiv model za izračun viskoznosti binarnih mešanic ogljikovodikov v okviru eksperimentalne napake v širokem območju tlaka (do 35 MPa).