

# EFFECT OF INTERFACIAL TENSION ON SOUND VELOCITY AND BULK MODULUS OF PETROLEUM FLUID MIXTURES

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**ABSTRACT:** Pore fluids and their volumetric properties have strong influence on the seismic properties of the porous rocks. The interfacial tension between liquid and gas phases of petroleum fluids may affect important properties of these fluids. The direct effect of this property is on capillary pressure which governs the vertical saturation of hydrocarbon into the pores of a reservoir rock. This effect is directly related to the radius of gas bubble suspended in the liquid phase (oil or water) which may leads to change in isentropic compressibility and the sound velocity in the petroleum fluids as well as the seismic properties of the rocks containing bubbly fluids. A modeling study is done to account the effects related to interfacial tension and gas bubble radius on the effective bulk modulus of compressibility of the bubbly fluids and the sound velocity. This modeling study was implemented on some real petroleum fluid mixtures. The results reveal that the presence of interfacial tension between the liquid-gas can decrease the values of effective bulk modulus and the sound velocity in bubbly fluids. This decrease is more pronounced in bubbly fluids confined in tight pores.

**Key Words:** Surface tension, seismic velocity, bubbly fluids, isentropic compressibility, rock physics

## INTRODUCTION

One of the primary goals of seismic exploration is to understand the type and composition of pore fluids at in-situ conditions. Various combinations of thermodynamic relationships, empirical formulas and experimental results are in practice to analyze the effects of formation fluids, their nature, composition, viscosity, compressibility, conductivity, temperature and pressure on seismic properties of porous rocks containing these fluids [1,2]. Many workers investigated the thermodynamic phase behavior and volumetric properties of these fluids [3,4] and their effects on the seismic properties of the hosting rocks [2,5-9]. All these studies deal with flat interfaces between liquid and gas phases. However, if the reservoir fluid is a bubbly liquid (mixture of oil/gas, water/gas), there exists a curve surface between the gas bubble and liquid, which produce capillary pressure. In seismic exploration, it is assumed that in surface seismic frequency limit the liquid and gas phases of formation fluids are under thermodynamic equilibrium [2], [4]. Experimental work indicates that the properties of porous rock and its forming-minerals influence the vapor liquid equilibrium (VLE) in porous media [10,11]. The main reason for this behavior is the existence of surface tension along the liquid-gas interface, which creates the pressure difference between the two-phases. Batzle and Wang [1] investigated the effects of pore fluid, its density, viscosity, temperature and pressure on seismic properties of pore fluids however they did not studied the impact of surface tension on all these parameters. Kieffer [12] studied the influence of capillary pressure for air-water mixtures to evaluate its possible effect on the mechanics of erupting volcanoes and geysers. Her results showed that for bubble radii smaller than 100 angstroms (1 angstrom =  $10^{-10}$  m), the surface tension is significant. This is the pore size (and therefore bubble size) found in shales and fine siltstones [13]. Surface tension of a fluid is an important transport property that not only reveals information on the structure and energetic region between two-phases but also exerts an important

influence on the transfer of mass and energy across the liquid/gas interface. Kelvin equation is used to find out liquid-gas phase equilibrium for fluids confined inside capillary tubes or porous media at low and intermediate pressure but it is not applicable for gas condensate because of their retrograde behavior. To overcome this problem Shapiro and Stenby [14], [15] derived a generalized modified form of Kelvin equation, which deals with non-ideal behavior of multi-components fluids. This derivation is based on the integration of the Clausius-Clayperon equation for fluids.

The bulk modulus of incompressibility of petroleum fluids and the sound velocity are widely used parameters in the exploration and production of petroleum reservoirs [1]. The sound velocity in fluids or, equivalently, its density and adiabatic bulk modulus, are primary input parameters in the fluid substitution models [2, 16]. Seismic properties of pore fluids have direct influence on the acoustic and seismic behavior of saturated rocks [2]. Newton-Laplace equation relates the thermodynamic properties of pure fluids to the acoustic properties of the fluids without porous media, whereas the Gassmann [5] or Biot [6] equations relate the thermodynamic properties of fluids to the acoustic properties of saturated rocks. In 1687, Newton developed the mathematical theory of acoustic propagation in pure fluid in which the compressibility of the fluid was taken as isothermal with internal heat flow. However, in 1816 Laplace effectively applied a simple principle that acoustic propagation in pure fluids is adiabatic without any internal heat flow. In other words, the entropy of the fluid remains constant at any interval of time. The important assumption – fluid under acoustic propagation is always in local thermodynamic equilibrium – establishes a link between thermodynamic properties of fluids and the seismic properties of the rock-forming minerals [2].

Fluid bulk modulus in two-phase liquid-gas state varies differently than in single phase either liquid or gas state. The reason is very large contrast in the fluid modulus of liquid

and gas. Many different methods have been proposed to determine the fluid modulus in single phase [17, 18]. However, less work has been done to find out fluid modulus in two-phase state. Nichita et al. [4] proposed a rigorous method to find out isentropic (adiabatic) compressibility (inverse of bulk modulus) in two-phase state. This method was applied on various petroleum mixtures and aqueous fluids by assuming flat interface between the liquid and gas bubbles. In two phase (liquid+gas) fluids gaseous phase is in the form of tiny gas bubbles, which are sparsely distributed into the liquid phase. Thus surface tension or interfacial tension exists between the walls of gas bubbles and liquid phase. Previously no work was done to find out the effect of the interfacial tension (IFT) on the fluid modulus and the sound velocity.

In this paper, we examined the effect of surface tension and bubble radius on the bulk modulus of compressibility and sound velocities of petroleum fluids in two phase state – between the bubble point ( $P_b$ ) and dew point ( $P_d$ ). A rigorous method proposed by Nichita *et al.* [4] is used with new thermodynamic equilibrium conditions under the effect of surface tension.

#### METHOD TO COMPUTE THE EFFECT OF GAS BUBBLE RADII ON ACOUSTIC PROPERTIES OF FLUIDS

Most of the reservoir fluids are complex mixtures of hydrocarbon and/or non-hydrocarbon components and can exist as a single-phase liquid, a single-phase gas or as a two-phase mixture depending on pressure ( $P$ ), temperature ( $T$ ) and composition ( $z$ ). The quantitative analysis of a two-phase system involves the determination of mole fractions of each substance present at given conditions into the gas and liquid phases. At low  $P$  and  $T$ , Raoult's law describes VLE of the ideal state mixtures, however, at high  $P$  and  $T$  where liquid and gases deviate from their ideal behavior, an equation of state (EoS) is used for this purpose (see for detail Whitson and Brulé [19]). VLE calculation is based on the fugacity (the measure of the chemical potential for transfer of a component from one phase to another) and the equilibrium ratios (ratio of the mole fraction of each  $i$  component in vapor phase to the mole fraction of each  $i$  component in the liquid phase).

A method proposed by Nichita et al. [4] is opted to compute the isentropic compressibilities and sound velocities of two-phase fluid systems in the absence of capillary forces between liquid and gas phases i.e. flat interface between the phases. This method is rigorous, versatile, requires only an isothermal or isobaric flash, which predict VLE and an expression of total enthalpy at given  $P$ - $T$ - $z$ .

It is assumed that all pores are filled with homogeneous fluid

#### Flash calculation

The isothermal two-phase flash calculation is required to define the solubility and composition of each fluid component in equilibrium phases at specified  $P$ ,  $T$ , and overall composition  $z$ , namely feed. The congenital hurdle in prediction of phase composition is lack of knowledge whether the mixture splits into two or more equilibrium phases or may exist as a single-phase at  $P$ - $T$  specifications. A multi-component fluid having composition vector  $\mathbf{n} =$

$(n_1, n_2, \dots, n_c)$ , (where  $n_c$  is the total number of components)

and  $z_i$  ( $\sum_{i=1}^{n_c} z_i = 1$ ) is the molar fraction of component  $i$  in

one mole of the feed is flashed at given  $P$ - $T$ . The schematic diagram of isothermal flash is shown in Figure 1. The feed  $z_i$  splits into two co-existing liquid and vapor phases with  $x_i$  and  $y_i$  mole fractions of liquid and vapor phase respectively.

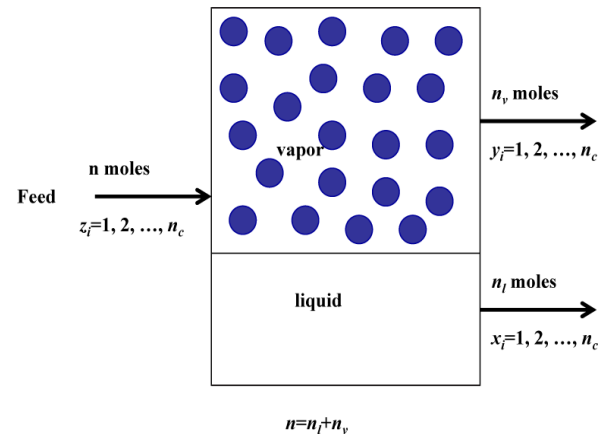


Figure 1: Schematic diagram of liquid-vapor isothermal flash.

For flat interface (*i.e.*, in the absence of capillary forces) between the co-existing liquid and vapor phases,  $P_l = P_g$ . This assumption might not hold if gas bubbles are of very small radius, or the curvature of the liquid/gas interface is larger, as is often the case with fluids confined in typical porous media. The critical properties ( $P_c$ ,  $T_c$  and  $w$ ) of each component are used as input in the isothermal flash calculation. Two parameters, Peng and Robinson [20] equation of state (PR EoS) is used to represent multi-component fluid behavior in both liquid and gas phases. The advantage of using PR EoS is its ability to accurately represent VLE using only critical properties and acentric factors of pure-components [3]. However, the PR EoS has limited capability in predicting saturated liquid densities, and is not accurate for highly polar systems such as aqueous fluids. Therefore, the composition distribution in aqueous and non-aqueous phases is estimated by using Soreide and Whitson [21] SW modifications in PR EoS.

#### Equilibrium conditions for curved interface

Consider a single spherical gas bubble of radius  $R_0$  is suspended in a liquid phase under hydrostatic equilibrium. Thus the pressure of the surrounding liquid phase ( $P_l$ ) is balanced by the gas pressure inside the bubble ( $P_v$ ). We suppose that gas inside the bubble behaves like an ideal gas, thus it follows the ideal gas law:

$$PV^\gamma = \text{const.} \quad (1)$$

where  $P$  is the pressure exerted on the gas bubble,  $V$  is the volume of gas bubble and  $\gamma$  is the ratio between specific heat capacities at constant volume ( $C_v$ ) and constant pressure ( $C_p$ ). For an adiabatic process  $\gamma = C_p/C_v > 1.0$ , however, for an isothermal process  $\gamma = 1.0$ .

The pressure of the liquid ( $P_l$ ) and gas ( $P_v$ ) phases is not equal and can be related by the Laplace equation [18], [22]:

$$P_c = P_v - P_l = 2\sigma \cos \varphi / R_0 \quad (2)$$

Where,  $P_c$  is the capillary pressure,  $\varphi$  is the angle of curvature. The wettability effects can be introduced by specifying the value of angle  $\varphi$ . It is supposed that liquid phase is completely wetting phase hence,  $\varphi$  is equal to zero and gas (vapor) phase is non-wetting phase then Eq. (2) is

$$P_v = P_l + 2\sigma / R_0 \quad (3)$$

It is clear from the above equation that the pressure inside the gas bubble increases with decrease in radius of bubble. Thus the density and bulk modulus of gas may increase substantially to smaller radii of bubbles.

The phase equilibrium between liquid and gas under the action of capillary forces implies that the fugacities of each component  $i$  should be equal in each phase (liquid and vapor) at different liquid and vapor pressures.

$$P_v = P_l + P_c \quad (4)$$

$$\mu_l^i(T, P_l, x) = \mu_g^i(T, P_v, y) \quad (5)$$

or

$$f_l^i(T, P_l, x) = f_g^i(T, P_v, y) \quad (6)$$

This equality can be obtained numerically by use of some measure of convergence, such as

$$\sum_{i=1}^{nc} \left[ \frac{f_l^i(T, P, x)}{f_g^i(T, P, y)} \right]^2 < 10^{-11} \quad (7)$$

It also holds that

$$\sum_{i=1}^{nc} x_i - 1 = 0 \quad (8)$$

$$\sum_{i=1}^{nc} y_i - 1 = 0 \quad (9)$$

$$z_i - x_i(1 - \theta_v) - y_i\theta_v = 0 \quad (10)$$

The equilibrium values of the fugacities and the chemical potential of each component in liquid and gas phase are computed at  $P_l$  and  $P_v$  respectively by using PR EoS for hydrocarbon fluids.

The well-known parachor correlation [23] is widely used in the petroleum industry to estimate the IFT between liquid-gas phases of pure fluid. Since in this study we are dealing with multi-component fluid systems therefore, the modified correlation by Weinaug and Katz [24] for hydrocarbon/hydrocarbon mixtures is used.

The above system of nonlinear equations (Eq. 5 – Eq. 10) is solved by using the Newton-Raphson iterative algorithm with controlled interval to prevent nonphysical values during the iterations.

The van der Waals mixing rules are used to calculate the attraction parameter  $a_{mk}$  and covolume  $b_{mk}$  of the mixture in each phase  $k$  in the cubic EoS.

$$a_{mk} = \sum_{i=1}^{nc} \sum_{j=1}^{nc} x_{ik} x_{jk} a_{ij} \quad (11)$$

$$b_{mk} = \sum_{j=1}^{nc} x_{jk} b_j \quad (12)$$

where  $x_{ik}$  is the mole fraction of component  $i$  in phase  $k$ , and

$$a_{ij} = a_{ji} = \sqrt{a_i} \sqrt{a_j} (1 - k_{ij}), \quad i, j = 1, n_c \quad (13)$$

$$a_i = \Omega_a \frac{R^2 T_{ci}^2}{P_{ci}} \alpha(T); \quad \alpha(T) = \left[ 1 + m(\omega_i) \left( 1 - \sqrt{T/T_{ci}} \right) \right]^2 \quad (14)$$

$$b_i = b_j = \Omega_b \frac{RT_{ci}}{P_{ci}} \quad (15)$$

in which  $T_{ci}$  and  $P_{ci}$  are the critical temperature and pressure of pure component  $i$  and  $k_{ij}$  the binary interaction parameters (BIPs) between components  $i$  and  $j$ . The values of  $\Omega_a$  and  $\Omega_b$  and the expression of  $m$  as a function of the acentric factor are specific for each EOS [4], [20]. The critical pressure, temperature and acentric factors of the fluid's components are taken from Reid et al. [25].

### Compressibility

The most important parameter in reservoir simulation is the isothermal compressibility. Therefore, the first and most important step after flash VLE prediction is to estimate the two-phase isothermal compressibility.

$$\beta_T^{2\phi} = -\frac{1}{V_t} \left( \frac{\partial V_t}{\partial P} \right)_T \quad (16)$$

where  $V_t = V_l + V_g$  is the total volume of one mole of input fluid.

Two-phase adiabatic compressibility can be written in terms of the two-phase isobaric thermal expansivity, two-phase apparent specific heat capacity and two-phase isothermal compressibility (Eq. 16):

$$\beta_S^{2\phi} = \beta_T^{2\phi} - TV_t \alpha_{2\phi}^2 / C_p^{2\phi} \quad (17)$$

or equivalently, the bulk modulus of two-phase fluid is

$$K_f^{2\phi} = 1 / \beta_S^{2\phi} \quad (18)$$

where the two-phase apparent isobaric heat capacity is defined as the partial derivative of total enthalpy with respect to temperature at constant pressure and composition.

### Sound velocity

After the computation of the adiabatic compressibility the sound velocity is calculated from the Newton-Laplace equation

$$v_{fl} = 1 / \sqrt{\rho_{fl} \beta_S} \quad (19)$$

where  $\rho_{fl} = \rho_l S_l + \rho_g S_g$  is the mixture density.

## RESULTS

The IFT effects on three chosen reservoir fluids (lighter hydrocarbon binary mixture, lighter-heavier hydrocarbon fluid and a natural gas mixture) are modeled. Algorithm described by Nichita et al. [4] is run with new equilibrium conditions at  $P_v = P_l + P_c$  as given in above section. The algorithm and its reliability in predicting the volumetric properties of multi-component hydrocarbon mixtures in single and two phases have been described elsewhere [2].

### Lighter hydrocarbon binary fluid mixture

A binary mixture of hydrocarbon fractions: methane ( $C_1$ ) and propane ( $C_3$ ) taken from Firoozabadi and Pan [3] is

studied at 327.6 K. The composition and other critical properties of this mixture are given in Table 1. The phase envelop of this binary mixture is shown in Figure 2. The isothermal flash is taken at constant temperature ( $T =$

Table 1: Composition and critical properties of 0.3C<sub>1</sub>/0.7C<sub>3</sub> mixture.

|                           | Molar composition | Critical temperature $T_c$ (K) | Critical Pressure $P_c$ (MPa) |
|---------------------------|-------------------|--------------------------------|-------------------------------|
| Methane (C <sub>1</sub> ) | 0.7               | 190.6                          | 4.6                           |
| Propane (C <sub>3</sub> ) | 0.3               | 369.8                          | 4.25                          |

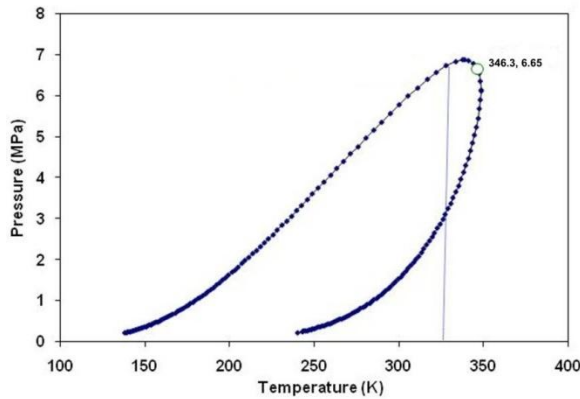


Figure 2: Phase diagram of lighter hydrocarbon mixture. The composition of the mixture is given in Table 1.

327.6 K). The critical temperature ( $T_c$ ) and critical pressure ( $P_c$ ) of this binary mixture are 346.3 K and 6.65 MPa respectively. It is assumed that the liquid phase is incompressible and the gas bubble radius is constant throughout complete flash i.e. independent of liquid saturation. The same temperature, pressure and composition specifications chosen by Firoozabadi and Pan [3] with radius of curvature equal to  $1.45 \times 10^{-8}$  m and  $\phi=0^\circ$  (liquid is totally wetting phase), give that the pressure of the vapor phase is higher than the liquid phase. The radius of curvature taken by Firoozabadi and Pan [3] can be found in very tight porous media with small porosity values. The surface tension is calculated by using the Parachor correlation. Our results are in good agreement with Firoozabadi and Pan [3]. We further modeled the IFT effects by taking radius of curvature of the dimension of typical pores. The estimated effect of surface tension and capillary pressure on the fluid bulk modulus ( $K_f$ ) and sound velocity ( $c$ ) at low gas saturation at ( $R_0=\infty, 1, 0.1, 0.01 \mu\text{m}$ ) are presented in Table 2. It is clear that in two-phase fluid, the bulk modulus of fluid increased (the sound velocity also increase) with increase in radius of curvature but this increase in  $K_f$  is so small that is quite difficult to observe in hydrocarbon exploration (Figure 3). A linear trend is noted between  $K_f$  and vapor pressure with regression coefficient  $R^2 \sim 0.99$ .

Table 2: IFT effect on the bulk modulus (Kf) and sound velocity (c) near bubble point of 0.3C<sub>1</sub>/0.7C<sub>3</sub> at T=327.6 K.

| $R_0$ ( $\mu\text{m}$ ) | $P_c$ (MPa) | $K_f$ (MPa) | $c$ (m/s) |
|-------------------------|-------------|-------------|-----------|
| $\infty$                | 0           | 4.51        | 118.1     |
| 1                       | 0.00034     | 4.53        | 119.4     |
| 0.1                     | 0.0034      | 4.557       | 121.1     |
| 0.01                    | 0.03408     | 4.59        | 123.2     |

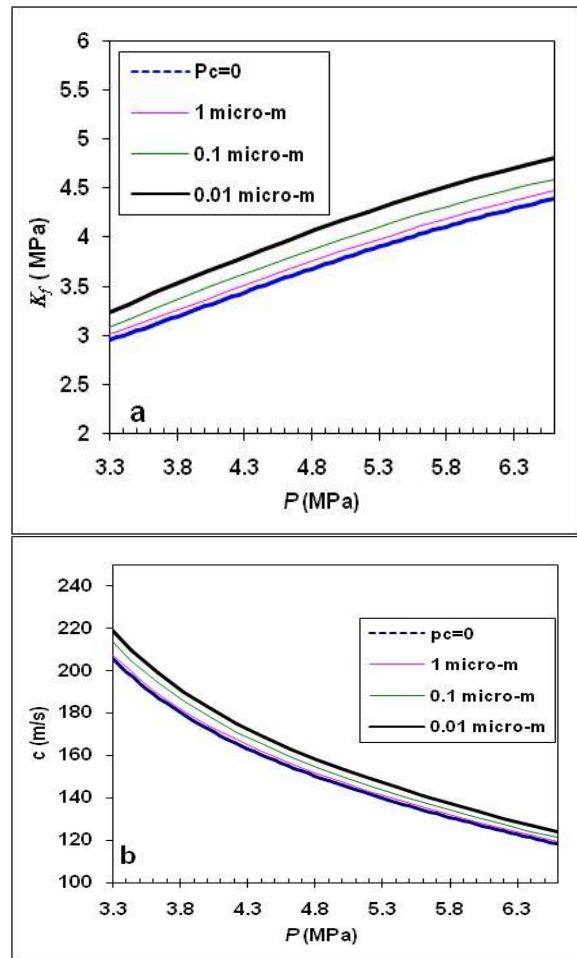


Figure 3: Effect of IFT on (a) bulk modulus and (b) sound velocity of light hydrocarbon mixture whose properties are given in Table 1.

**Lighter-heavy hydrocarbon fluid mixture**

In second numerical example, we deal with a binary fluid of methane (lighter) and hexane (heavier) hydrocarbon fraction at  $T = 310$  K and bubble radii ( $R_0=\infty, 1, 0.1, 0.01 \mu\text{m}$ ). The critical properties and composition of this fluid are given in Table 3. The phase diagram of this binary mixture is given in Figure 4. The IFT effects on the two phase bulk modulus and sound velocity in two-phase ( $P_d < P < P_b$ ) region are illustrated in Figure 5. In this figure, the effects of IFT on the fluid modulus and the sound velocity are observable, although they are not pronounced. This small change is not observable in field measurements. From figure, it is also clear that gas phase pressure increases with increase in bubble radius. Phase behavior changes due to surface tension and capillary pressure effects. However, it does not change the shape of the bulk modulus and sonic velocity curves.

Table 3: Composition and critical properties of C<sub>1</sub>-C<sub>6</sub> mixture.

|                           | Molar composition | Critical Temperature $T_c$ (K) | Critical Pressure $P_c$ (MPa) |
|---------------------------|-------------------|--------------------------------|-------------------------------|
| Methane (C <sub>1</sub> ) | 0.4               | 190.6                          | 4.6                           |
| Hexane (C <sub>6</sub> )  | 0.6               | 507.4                          | 2.97                          |

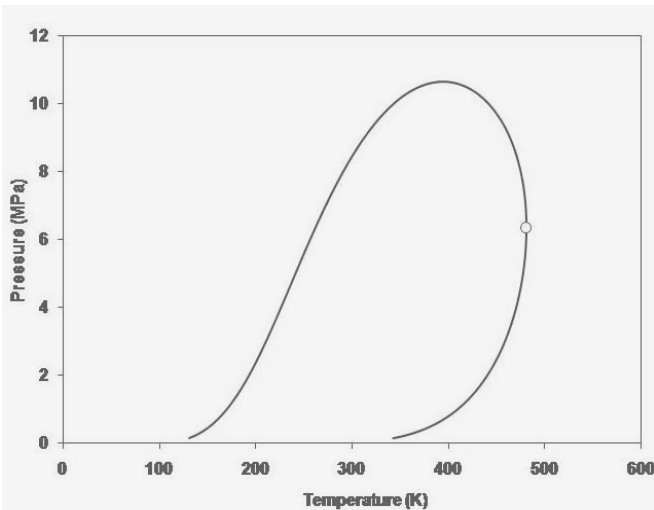


Figure 4: Phase envelop of lighter (C1)-heavy (C6) hydrocarbon fluid mixture. The properties of this mixture are given in Table 3.

**DISCUSSION AND CONCLUSIONS**

We studied different multi-component reservoir fluids including some reservoir oils and gas systems, to integrate the capillary effects on phase behavior, bulk modulus and sound velocity in two phase fluids. For hydrocarbon fluid systems, PR EOS and Lee-Kesler [26] mixing rule are used. We developed FORTRAN codes for isothermal flash calculation and two-phase compressibility estimation. The algorithm described by Nichita *et al.* [4] is used with new equilibrium conditions under the action of capillary pressure which is a function of gas bubble radius. To check the validity of the codes we tested it on two hydrocarbon systems as taken by Firoozabadi and Pan [3]. Our results are in close agreement with of Firoozabadi and Pan [3]. To make our problem more realistic, we have taken the radii of gas bubbles in the order of pore dimension encountered in real porous media. The capillary pressure, the equilibrated compressibility and the sound velocity calculated in two-phase petroleum fluids. The fluid modulus decreases with increase in bubble radius. However, this decrease is very small. The sound velocity also decreases with increase in bubble radius. This decrease in bulk modulus and sound velocity is large for very small bubbles (bubble radius < 0.01 micro-meter). Phase behavior changes due to surface tension and capillary pressure affects. However, it doesn't change the shape of the fluid modulus and sound velocity curves in two-phase state.

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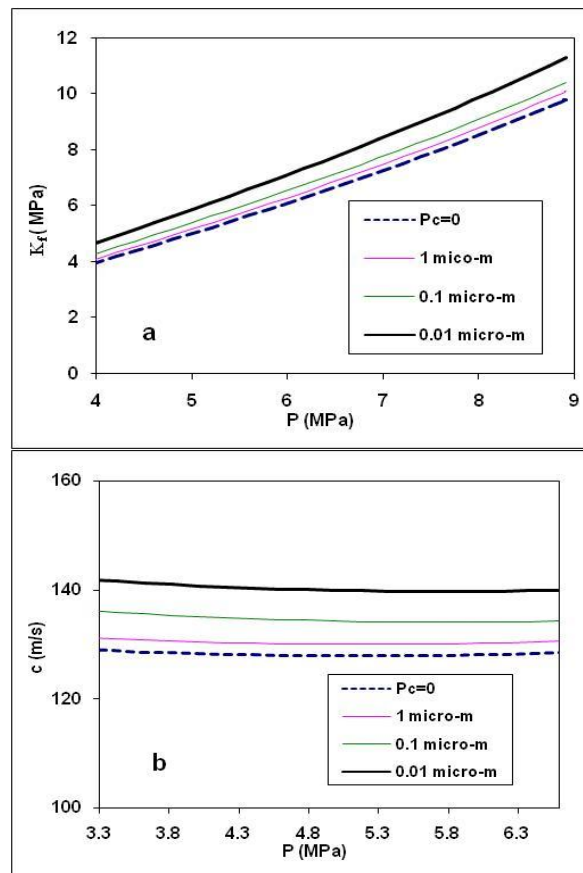


Figure 5: Effect of IFT on (a) bulk modulus and (b) sound velocity of light-heavy hydrocarbon mixture whose properties are given in Table 3.

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