

Estimation of internal pressure of liquids and liquid mixtures

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ABSTRACT

By combining the van der Waals' equation of state and the Free Length Theory of Jacobson, a new theoretical model is developed for the prediction of internal pressure of pure liquids and liquid mixtures. It requires only the molar volume data in addition to the ratio of heat capacities and critical temperature. The proposed model is simple, reliably accurate and capable of predicting internal pressure of pure liquids with an average absolute deviation of 4.24% in the predicted internal pressure values compared to those given in literature. The average absolute deviation in the predicted internal pressure values through the proposed model for the five binary liquid mixtures tested varies from 0.29% to 1.9% when compared to those of literature values.

Keywords:

van der Waals; pressure of liquids; theory of Jacobson; capacity of heat liquids; equation of Srivastava and Berkowitz

1. INTRODUCTION

The importance of internal pressure in understanding the properties of liquids and the full potential of internal pressure as a structural probe did become apparent with the pioneering work of Hildebrand^{1,2} and the first review of the subject by Richards³ appeared in 1925. In an excellent article Dack⁴ reviewed the importance of solvent internal pressure and cohesion to solution phenomena. A review on the relationship between the intermolecular forces and properties of solution was made by Kortum⁵.

Barton⁶ discussed the relationship between internal pressure and molar volume in some depth. Pointing out that internal pressure is a uniquely important parameter in sonochemistry, Srivastava and Berkowitz⁷ developed an expression, which permits the evaluation of internal pressure from readily available and easily measurable quantities. In this work a simple equation is proposed by incorporating the Free Length Theory of Jacobson^{8,9} and van der Waals' equation of state; the proposed model is a purely predictive tool for predicting internal pressure of liquids and liquid mixtures. Computed internal pressure values for liquids and liquid mixtures through the proposed equation are compared with those of literature.

2. PREVIOUS WORK

Starting from the van der Waals equation of state

$$P + (a/V^2) = RT / (V-b)$$

With P = pressure
 V = molar volume
 R = universal gas constant
 T = temperature
 a and b = van der Waals' constants,
 Srivastava and Berkowitz⁷ arrived at

$$u^2\rho = (\gamma_L b / RT) \pi_i^2 \quad (1)$$

where u = ultrasonic velocity
 ρ = density
 γ_L = ratio of heat capacities of liquid

And π_i = internal pressure

Replacing b, in terms of M and ρ, in eqn. [1] they obtained an expression for internal pressure of a liquid:

$$\pi_i = u\rho / M^{1/2}k \quad (2)$$

Where M = molar mass of liquid

Present Work

1. Estimation of Internal Pressure using the Srivastava – Berkowitz equation

Having fitted the experimental π_i , u and ρ values in Eqn. (2), Srivastava and Berkowitz obtained the constant (k) values for a few families of organic compounds. The reported k_{SB} (known as Srivastava and Berkowitz constant) values directly yield π_i values in atmospheres, provided u and ρ are in c.g.s. system of units. When one is to use SI system of units.

$$\pi_i = u\rho / 10 k_{SB} M^{1/2} \quad (\text{in atm}) \quad (3)$$

or
$$\pi_i = 10^3 \times 101.325 [u\rho / (10 k_{SB} M^{1/2})] \quad (\text{in Pa}) \quad (4)$$

2. Internal Pressure from u, ρ and γ_L

Consider Eqn. (1)

$$u^2\rho = (\gamma_L b / RT) \pi_i^2$$

Approximating that $b \approx M / 4\rho$ and simplifying, Eqn. (1) becomes

$$\pi_i = 2u\rho (RT)^{1/2} / (\gamma_L M)^{1/2}$$

This can be shown to be equal to

$$\pi_i = (1 / 555.613) (u\rho / M^{1/2}) (T / \gamma_L)^{1/2}$$

$$\text{i.e., } \pi_i = (1.7998 \times 10^{-3}) (u\rho / M^{1/2}) (T / \gamma_L)^{1/2} \quad (\text{in atm}) \quad (5)$$

$$\text{or } \pi_i = 182.3656 (u\rho / M^{1/2}) (T / \gamma_L)^{1/2} \quad (\text{in Pa}) \quad (6)$$

(Note u and ρ are in SI units)

Eqns. (5) and (6) are useful in predicting internal pressures when k_{SB} values are not available and when u , ρ and γ_L are known, Eqn. (5) and (6) describe k_{SB} in terms γ_L and T . For example from Eqn. (5) one can show that

$$k_{SB} \text{ in SI units} = 555.613 (\gamma_L / T)^{1/2} \quad (7)$$

3. New Model Development

$$u^2\rho = (\gamma_L b / RT) \pi_i^2 \quad (1)$$

This is the starting point for developing a new expression here. It can be written as

$$\pi_i = u\rho^{1/2} / (\gamma_L b / RT)^{1/2} \quad (8)$$

Jacobson's⁸ definition for free length is

$$L_f = 2V_a/Y \quad (9)$$

where V_a = available molar volume = $V - V_0$

V = molar volume at a given temperature

V_0 = molar volume at absolute zero temperature (0 K)

and Y = molar surface area of the molecules = $(36\pi NV_0^2)^{1/3}$

According to Jacobson's free length theory, free length, L_f and adiabatic compressibility, β ($= 1 / u^2\rho$) are related by

$$L_f / \beta^{1/2} = (u^2\rho)^{1/2} L_f = u\rho^{1/2} L_f = K \quad (10)$$

K , in Eqn. (10) is the Jacobson constant and it is temperature dependent. Replacing L_f in Eqn.(10) by molar volumes and molar surface area of the molecules as per Eqn. (9), Eqn. (10) can be written as

$$u\rho^{1/2} = K Y / 2V_a \quad (11)$$

In the light of Eqn. (11), Eqn. (8) turns out to

$$\pi_i = K Y / 2V_a (\gamma_L b / RT)^{1/2} \quad (12)$$

Approximating that

$$b \approx V / 4 \quad (13)$$

Eqn. (12) reduces to

$$\pi_i = K Y / 2V_a V^{1/2} (\gamma_L / 4RT)^{1/2} = K Y / 2V_a V^{1/2} k_{\text{SBSI}}, \quad (\text{in kg / ms}^2) \quad (14)$$

With $k_{\text{SBSI}} = (\gamma_L / 4RT)^{1/2}$, (in (kgmol / kg)^{1/2} s / m)

It can be shown that

$$k_{\text{SBSI}} = 555.613 (\gamma_L / T)^{1/2}, \quad (\text{in (kg kmol)}^{1/2} / \text{m}^2 \text{s atm}) \\ = 10 k_{\text{SB}}$$

Eqn. (14) is the new equation proposed in this work for the estimation of internal pressure from pure component properties, particularly, from molar volumes. As derived, the new equation is the result of a combination of the van der Waals' equation of state and the Free Length Theory of Jacobson^{8,9}.

The various quantities required to use Eqn. (14) are described below

$$K = K_J \times 10^{-10}, \quad (\text{m kg})^{1/2} / \text{s}$$

$$K_J = \text{Jacobson's constant in kg}^{1/2}(\text{A}^0) / \text{m}^{1/2} \text{s} = 18687 + 40.391 t \text{ (}^\circ\text{C)} \text{ (Reference 10)}$$

$$Y = (36\pi N V_0^2)^{1/3} = [36\pi (6.023 \times 10^{26})]^{1/3} V_0^{2/3} \\ = 4.084 \times 10^9 V_0^{2/3}, \quad (\text{in m}^2 / \text{kg mol}), \quad V_0 \text{ in m}^3 / \text{kg mol}$$

$$V_0 = V [1 - (T / T_c)]^{0.3} = V (1 - T_r)^{0.3}, \quad V \text{ in m}^3 / \text{kg mol}$$

$$V_a = V - V_0, \quad V_a \text{ in m}^3 / \text{kg mol}$$

And $R = 8314.3$, (in kg m² / kg mol s² K)

With the above Eqn. (14) is

$$\pi_i = (K_J \times 10^{-10}) (4.084 \times 10^9) V_0^{2/3} (8314.3)^{1/2} / V_a V^{1/2} (\gamma_L / T)^{1/2} \quad (\text{in kg/ms}^2) \quad (15)$$

Eqn. (15) in terms of K , k , T_c and V turns to

$$\pi_i = 37.239 K_J (1 - T_r)^{0.2} T^{1/2} / V^{5/6} [1 - (1 - T_r)^{0.3}] \gamma_L^{1/2} \quad (\text{in kg / ms}^2) \quad (16)$$

eqn. (16), the work form of the new equation, involves only K_J , γ_L , T , T_c and V .

3. RESULTS AND DISCUSSIONS

The new equation, Eqn. (14) or its work form, Eqn. (16) requires molar volume data and critical temperature data in addition to the ratio of liquid heat capacities, while the equation of Srivastava and Berkowitz⁷ requires molar volume and ultrasonic velocity data and, of course the Jacobson constant is required in the newly derived equation. Eqn. (14), proposed in this work, permits evaluation of internal pressure from the Jacobson constant, the Srivastava-Berkowitz group parameter and molar volume data. The equation can readily be extended to multicomponent mixtures.

Internal pressure values were computed for nineteen liquids through the proposed equation, Eqn. (14) and through the Srivastava and Berkowitz equation, Eqn. (3). As shown in Table 1, the proposed model is capable of predicting internal pressure of pure liquids with an average absolute deviation of 4.24% in the predicted internal pressure values compared to those by the Srivastava-Berkowitz equation.

Table 1. Internal Pressure Values of Liquids at 298.15K using the Proposed Method

S. No	Liquid	Density	Molar Volume	Ultrasonic Velocity	Critical Temp	Available Volume	k_{SB}	Internal Pressure, atm Proposed
		$\times 10^{-3}$	$\times 10^6$			$\times 10^6$		
		kg/m ³	m ³ /kg·mol	ms ⁻¹	K	m ³ /kg·mol		
1	n-Hexane	0.6551	131.55	1083	507.4	30.70	3.64	2157.59
2	n-Heptane	0.6799	147.38	1133	540.2	31.54		2175.63
3	n-Octane	0.6988	163.47	1170	568.8	32.65		2164.90
4	2,2,4-Trimethylpentane	0.6878	166.08	1077	543.9	35.22		1991.09
5	n-Nonane	0.7148	179.43	1212	594.6	33.81		2142.58
6	n-Decane	0.7267	195.80	1222	617.6	35.13		2107.67
7	n-Dodecane	0.7460	228.34	1288	658.3	37.13		2032.91
8	n-Tetradecane	0.7599	258.43	1302	694.0	40.06		1974.35
9	n-Hexadecane	0.7713	293.59	1322	717.0	43.73		1856.44
10	Benzene	0.8742	89.35	1304	562.1	18.13	4.00	3198.86
11	Toluene	0.8627	106.81	1309	591.7	20.26		2982.27
12	m-Xylene	0.8602	123.42	1326	617.0	22.17		2813.42
13	Mesitylene	0.8615	139.52	1346	637.3	24.05		3020.73
14	1-Propanol	0.8000	75.12	1204	536.7	16.22	3.29	4176.97
15	2-Propanol	0.7812	76.93	1141	508.3	17.91		3744.07
16	1-Butanol	0.8059	91.98	1240	562.9	18.63		3805.05
17	2-Methyl-1-propanol	0.7932	92.86	1191	536.0	20.09		3493.08
18	1-Pentanol	0.8112	108.67	1277	586.0	20.87		3521.18
19	1-Heptanol	0.8179	141.76	1330	633.0	24.65		3163.43

Density and ultrasonic velocity data have been taken from the literature [12]

Table 2. Estimated Internal Pressure Values at 298.15 K Through the Two Methods (The Srivastava – Berkowitz Method and the Newly Proposed Method)

S. No	Liquid	Ref.	Molar	Ultrasonic	Available	Gama, γ_L	k_{SB}	Internal Pressure, atm		
			Volume	Velocity	Volume	Calculated		Calculated	Dack	Proposed
			$\times 10^6$		$\times 10^6$					
			m ³ /kgmol	ms ⁻¹	m ³ /kgmol				[4]	Eqn.
1	Acetone	[13]	74.05	1150.0	17.24	1.699	4.195	3323.85	3019.0	
2	Acetonitrile	[13]	52.81	1288.0	11.08	1.657	4.142	3839.97	4584.8	
3	Benzene	[13]	89.40	1306.5	18.13	1.620	4.100	3736.75	3445.3	
4	tert-Butyl alcohol	[14]	94.91	1123.2	22.21	2.019	4.573	3344.49	2237.7	
5	Carbon disulphide	[15]	60.63	1140.9	26.08	1.638	4.119	3716.10	4157.1	
6	Carbontetrachloride	[13]	97.06	927.0	19.95	1.535	3.987	3402.30	2938.2	
7	Choloroform	[13]	80.75	983.0	17.44	1.692	4.187	3645.91	3077.0	
8	Ethylene glycol	[14]	55.91	1655.9	9.49	1.493	3.932	4954.80	5884.2	
9	n-Hexane	[16]	31.59	1076.4	31.20	1.493	3.932	2357.66	1989.7	
10	1-Propanol	[14]	75.15	1216.3	16.22	1.528	3.978	2840.75	3441.7	
11	2-Propanol	[17]	60.68	1204.8	14.12	1.647	4.129	2766.43	3622.8	
12	Toluene	[18]	106.88	1303.7	20.26	1.314	3.689	3501.39	3220.8	
Average absolute percentage deviation									12.06	

Table 2 contains the calculated γ_L and k_{SB} values as well as the computed internal pressure values through the use of Srivastava-Berkowitz equation and the proposed equation. When compared with literature values⁷ for twelve liquids considered in Table 2, the average absolute deviations in the predicted internal pressure values are 10.74% (the Srivastava-Berkowitz equation) and 12.06% (proposed equation), showing the performance-characteristics of these equations. The purely predictive nature of the proposed equation has to be considered at this juncture.

The applicability of the proposed equation in predicting the internal pressures of liquid mixtures was ascertained by using the data of five liquid mixtures, trichloroethylene + benzene / carbon tetrachloride / chloroform / toluene / p-xylene for which the results on the Srivastava-Berkowitz equation are available¹¹; nearly identical results were obtained. The calculated and predicted internal pressure values were obtained. The calculated and predicted internal pressure values through the Srivastava-Berkowitz equation and the new equation of this study are given in Table 3. The average absolute percentage deviation in predicted internal pressure values for the five liquid mixtures shown in Table 3, varies from 0.29 to 1.91% in comparison with those given by Srivastava-Berkowitz equation⁷.

Table 3. Internal Pressure from various methods at 303.15 K.

Trichloroethylene – Benzene										
x_1	0.1112	0.2565	0.3679	0.5456	0.6064	0.7435	0.9459			Average absolute percentage deviation 0.29
Srivastava-Berkowitz Eq., π_i (atm)	3651.1	3644.3	3631.7	3629.2	3630.9	3635.8	3624.4			
Newly Proposed Eq. π_i (atm)	3642.5	3634.5	3630.1	3624.2	3622.5	3619.5	3601.1			
Absolute percentage deviation	0.24	0.27	0.04	0.14	0.23	0.45	0.64			
Trichloroethylene – Toluene										
x_1	0.1256	0.2537	0.6721	0.7233	0.9395					Average absolute percentage deviation 0.73
Srivastava-Berkowitz Eq., π_i (atm)	3510.0	3551.9	3584.0	3593.9	3628.3					
Newly Proposed Eq. π_i (atm)	3561.4	3596.4	3596.1	3599.4	3612.5					
Absolute percentage deviation	1.46	1.25	0.34	0.15	0.44					
Trichloroethylene – p-Xylene										
x_1	0.2137	0.2299	0.3990	0.5717	0.6011	0.7598				Average absolute percentage deviation 1.91
Srivastava-Berkowitz Eq., π_i (atm)	3400.1	3413.2	3454.0	3490.6	3501.3	3552.6				
Newly Proposed Eq. π_i (atm)	3491.1	3494.1	3524.2	3553.8	3558.9	3584.7				
Absolute percentage deviation	2.68	2.37	2.03	1.81	1.64	0.90				
Trichloroethylene – Chloroform										
x_1	0.2299	0.3399	0.4665	0.6863	0.7221	0.8367	0.9303			Average absolute percentage deviation 1.63
Srivastava-Berkowitz Eq., π_i (atm)	3592.8	3599.2	3604.9	3631.3	3629.4	3632.2	3647.6			
Newly Proposed Eq. π_i (atm)	3504.5	3521.6	3540.7	3576.8	3578.2	3593.7	3608.9			
Absolute percentage deviation	2.46	2.15	1.78	1.50	1.41	1.06	1.06			
Trichloroethylene – Carbon tetrachloride										
x_1	0.1343	0.2258	0.3196	0.4385	0.6352	0.7258	0.8319	0.9439		Average absolute percentage deviation 0.95
Srivastava-Berkowitz Eq., π_i (atm)	3381.9	3306.5	3350.8	3403.4	3485.5	3526.3	3573.3	3622.6		
Newly Proposed Eq. π_i (atm)	3262.7	3298.1	3334.8	3382.7	3464.2	3502.9	3549.1	3595.6		
Absolute percentage deviation	3.52	0.26	0.48	0.61	0.61	0.66	0.68	0.74		

4. CONCLUSION

A new method was developed for the prediction of internal pressure of pure liquids and liquid mixtures. This theoretical model combines the Free Length Theory of Jacobson and van der Waals' equation of state. It requires only the molar volume data in addition to the ratio of heat capacities and critical temperature. The model is simple and reliably accurate. The predictive ability of the new equation was tested by comparing the internal pressure values obtained through this equation with those of the Srivastava-Berkowitz equation.

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