

Excess Internal Pressure of (diethyl carbonate + n-decane) Mixture at Two Different Temperatures

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Abstract

Internal pressure is an important tool for study of intermolecular interactions in liquid mixtures. Therefore prediction of internal pressure and its corresponding excess parameters are very important. The different liquid systems have different degrees of cohesion and this cohesive force creates a pressure which is directed inwards. The mole fraction additivity and volume fraction additivity of internal pressure for the ideal mixture is not same. In this work, a comparative study has been made for the excess internal pressure for diethyl carbonate and n-decane mixtures at a temperature 298.15K and 308.15K.

Introduction

Excess internal pressure and internal pressure is very important parameters for studying the intermolecular interactions between liquids and liquid mixtures and it has been found to be a very important tool in the theory of liquid state in explaining various characteristics of liquids like clustering phenomenon, internal structure, ordered structure, etc. Thermodynamical methods provide a very accurate method for estimation of internal pressure of liquid and liquid mixtures. The importance of internal pressure in liquid mixtures was recognized long ago by several workers like by Hildebrand and Scott [1] etc. As we know that molecular interactions in liquid mixtures are discussed in terms of excess internal pressure. The additivity of mole fraction scale for internal pressure is quite often erroneously assumed for an ideal mixture. In present work a corrected and modified formula for the computation of excess internal pressure is used and compared with the old method. In this work the additivity of volume fraction scale is taken for computation of internal pressure of the liquid mixture. For this, mixture of diethyl carbonate and n-decane at temperature 298.15 and 303.15 K has been put to test.

Theory

Internal pressure(P_{int}) is thermodynamically defined in terms of internal energy and molar volume of real fluids as

$$P_{int} = \left(\frac{\partial U}{\partial V} \right)_T \quad (1)$$

Where U is the internal energy, V is the volume and T the temperature.

Assuming a thermodynamic equation as

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P \quad (2)$$

where P is the pressure.

Employing the expression of thermal expansion coefficient(α) and isothermal compressibility(κ_T), internal pressure can be expressed as[2]

$$P_{int} = \left(\frac{\partial U}{\partial V} \right)_T = \left(\frac{\alpha T}{\kappa_T} - P \right) \quad (3)$$

where all the symbols have their usual meaning.

The excess internal pressure, P_{int}^E of liquid mixture is given by

$$P_{int}^E = P_{int} - P_{int}^{id} = P_{int} - \sum P_{int_i} \cdot x_i \quad (4)$$

Where x is mole fraction and id denotes the ith component and the ideal mixture.

W Marczak[3] developed an idea for calculating excess internal pressure using mole fraction additivity in thermal expansion coefficient and isothermal compressibility which is not very accurate method since both thermal expansion coefficient and isothermal compressibility are volume fraction additive quantities[4].

For the calculation of P_{int}^{id} , various authors have assumed [4-7] that $P_{int}^{id} = \sum P_{int}^* x_i$

which is erroneously but in present work P_{int}^{id} may be given as

$$P_{int}^{id} = \left(\frac{\alpha^{id} T}{\kappa_T^{id}} - P \right) \quad (5)$$

where

$$\alpha^{id} = \sum \phi_i \alpha_i \quad \text{and} \quad \kappa_T^{id} = \sum \phi_i \kappa_{Ti}$$

And
$$\phi_i = \frac{x_i V_i}{\sum x_i V_i}$$

where ϕ_i is the volume fraction. Now from eqn 5 we have

$$P_{int}^{id} = \frac{\sum \phi_i \alpha_i T}{\sum \phi_i \kappa_{Ti}} - P \quad (6)$$

using eqn 3 & eqn 6 in eqn 4 we have

$$P_{int}^E = \left(\frac{\alpha T}{\kappa_T} - P \right) - \left(\frac{\sum \phi_i \alpha_i T}{\sum \phi_i \kappa_{Ti}} - P \right) \quad (7)$$

$$P_{int}^E = \left(\frac{\alpha T}{\kappa_T} - \frac{\sum \phi_i \alpha_i T}{\sum \phi_i \kappa_{Ti}} \right) \quad (8)$$

where thermal expansion coefficient and isothermal compressibility have been computed through recently developed relation [8-10].

Results and Discussion

The value of excess internal pressure of diethyl carbonate + n-decane mixtures of at 298.15 and 303.15 K have been calculated using eqn-4 and eqn-8 (Table-1). Necessary data needed for the calculation have been taken from the literature[11]. The excess internal pressure obtained via the two methods (eq-4 & eq-8) have been plotted graphically with excess volume (Graph-1). At the two different temperatures under the investigation we find that the graph shows less deviation, calculated by (eq-8). While the excess internal pressure values obtained from the previous method (eq 4) show more deviation, when compared with excess volume.

Under investigation, the excess internal pressure values obtained via eq-8 are found to be very near to excess volume. It is a well known fact that the excess volume indicates correct information about interactions. These literature values further proves the validity of the modified and the corrected expression for evaluation of excess internal pressure as compared to the one proposed earlier[3]. Further, it also proves that the excess internal pressure computed with the mole fraction additivity (eq-4) is definitely erroneous, since the values of excess internal pressure obtained from eq-4 indicate more deviation.

References

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Table-1 Excess Internal pressure of binary liquid mixture**Dimethyl carbonate + n-decane at 298.15K**

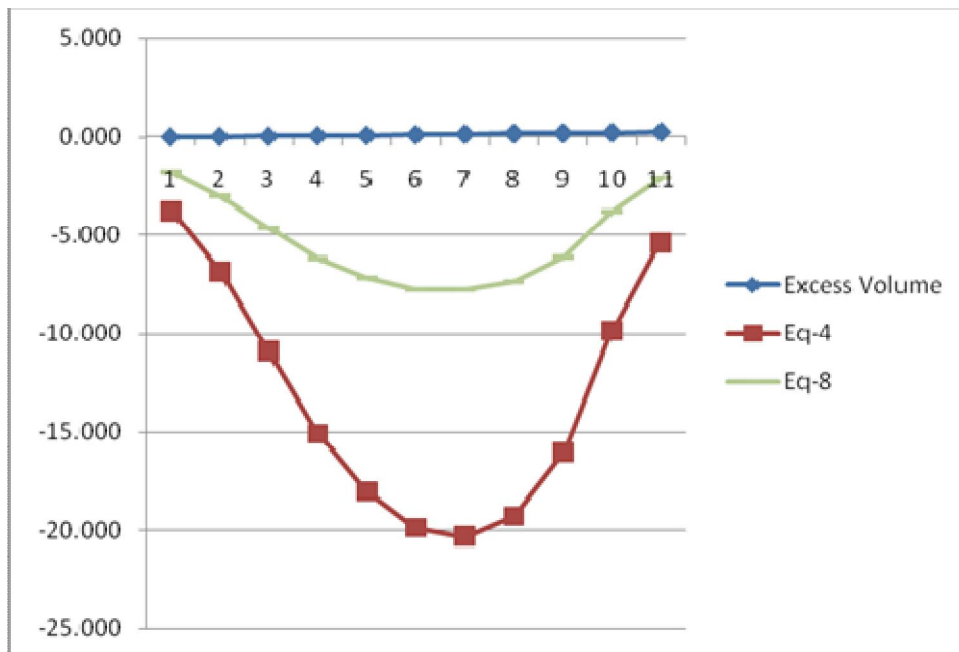
x1	d(mix)	u(mix)	VE	PintE	PintE
	gm cm ⁻³	m s ⁻¹	cm ³ /mol	atm(Eq-4)	atm(Eq-8)
0.0575	0.7339	1225.70	0.000	-3.76	-1.78
0.1132	0.7420	1218.60	0.017	-6.85	-3.05
0.1958	0.7550	1208.70	0.031	-10.92	-4.67
0.3010	0.7733	1197.50	0.058	-15.13	-6.22
0.4012	0.7927	1188.30	0.073	-18.06	-7.19
0.5007	0.8140	1180.50	0.108	-19.89	-7.77
0.6033	0.8386	1174.20	0.134	-20.34	-7.79
0.6998	0.8645	1169.80	0.162	-19.31	-7.40
0.8000	0.8949	1167.80	0.183	-16.09	-6.17
0.9013	0.9299	1169.40	0.210	-9.87	-3.78
0.9514	0.9490	1171.90	0.243	-5.41	-2.07

Dimethyl carbonate + n-decane at 308.15K

x1	d(mix)	u(mix)	VE	PintE	PintE
	gm cm ⁻³	m s ⁻¹	cm ³ /mol	atm(Eq-4)	atm(Eq-8)
0.0450	0.7245	1189.00	0.000	-2.87	-1.37
0.0984	0.7321	1179.50	0.035	-6.72	-3.55
0.1989	0.7474	1169.20	0.050	-11.10	-5.06
0.2983	0.7644	1158.50	0.096	-15.06	-6.63
0.3998	0.7835	1149.00	0.113	-18.12	-7.79
0.4996	0.8046	1141.00	0.158	-19.96	-8.43
0.6002	0.8282	1134.70	0.201	-20.47	-8.53
0.6982	0.8542	1130.30	0.242	-19.34	-8.00
0.8015	0.8850	1128.30	0.278	-16.01	-6.63
0.9020	0.9193	1129.80	0.308	-9.85	-4.11
0.9522	0.9384	1132.20	0.330	-5.35	-2.23

Graph-1 Variation of Excess Internal Pressure with Excess volume

Dimethyl carbonate + n-decane at 298.15K



Graph for Excess Internal Pressure

Dimethyl carbonate + n-decane at 308.15K

