Redlich-Kwong Equation of State Used For Prediction phase Data.

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Abstract:

The solubility of CO_2 in the non-volatile compounds of *n*-Hexadecane, Diphenylmetnane, Diphenyl ethane, Ethyl benzene and of Nitrogen in *n*-Hexadecane, at temperature range 298.15-358.15 K are measured at partial pressure of one atmosphere, Falling-film flow technique was used in the present experimental work.

It is seen that in most cases the solubility is decreased at the temperature increased, though in the case of the Nitrogen/n-Hexadecane system the reverse is true. The effect is probably related to the decrease in solvent density which occurs as the temperature raises. For systems of low Solubility ,this effect tends to counter balance the increase tendency for solute molecules to "escape" from the solvent, arising from their increase kinetic energy **.** In addition ,the binary interaction constant (L_{AB}) was calculated by fitting the mole fraction solubility of solute gases CO_2 and N_2 by using Redlich-Kwong equation of state for predicting phase data. The interaction constant L_{AB} was calculated from the following expression:

$$L_{AB} = 1 - a_{AB}(a_A a_B)^{-0.5} \text{.....(1)}$$

Key-Words / Equation of state, phase behaviour, carbon dioxide.

الخلاصة:

تـم قيـاس ذوبانيـة ثاني اوكسيد الكاربـون (Co_2) في المركبـات غير المتطايـرة Diphenylmetnane – *n*-Hexadecane , Ethylbenzene , Diphenylethane والنتروجين (N_2) في n – Hexadecane في درجات حرارية مختلفـة (298.15 – 358.15) تحت ضغط جزئي (1) جو.

لقد استخدم تكنيك ((السقوط الحر)) للسائل في وسط غازي في حالة اتزان .

تبين معظم حالات التجارب , حصول تناقص ذوبانية الغاز (co_2) كلما ارتفعت درجات الحرارة , عدى حالة غاز النيتروجين في المذيب n – Hexadecane حيث تكون العكس هو الصـحيح بسبب انخفاض كثافة المذيب, نتيجة ارتفاع درجات الحرارة . فعندما تكـون الذوبانيـة واطئـة يحصل تأثير في التوازن (السلوك الطوري) مما يؤدي الى تحرر جزيئات المذاب مـن المـذيب وهذا يؤدي الى زيادة في الطاقة الحركية.

اضافة الى ذلك تم حساب (L_{AB}) ثابت التجاذب بين جزيئات المذاب والمـذيب بهـدف تثبيت الكسر المولي لذوبانية الغـازات المذابـة (CO_2) و (N_2) باسـتخدام معادلـة الحالـة (Redlich – Kwong) للتنبؤ الطوري.

تم حساب ثابت التجاذب (L_{AB}) باستخدام المعادلة الاتية

$$L_{AB} = 1 - a_{AB}(a_A a_B)^{-0.5} \text{ …….. (1)}$$

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Introduction:

The knowledge of the solubility of gases in liquids of low volatility and vapor-liquid equilibrium are frequently required in the design and operation of separation processes.

Although the Redlich-Kwong equation of state (4) is comparatively simple in form .It is able to provide a fairly accurate representation of the volumetric behaviour of both the liquid and vapor phases**.** It has been used by many authors (2, 5, 6). The original equation is as follows:

$$P = \frac{RT}{v-b} - \frac{a}{T^{0.5}v(v+b)} \quad \text{.....(2)}$$

The parameters *a* and *b* were originally taken to be independent of temperature and pressure, being given for pure components by the following expressions:

$$a = 0.4278 \ \frac{R^2 T_c^{2.5}}{P_c} \quad \text{.....(3)}$$

and:

$$b = 0.0867 \ \frac{RT_c}{P_c} \quad \text{..... ..(4)}$$

The Redlich-Kwong equation of state gives reasnable description of the volumetric properties not only of pure components but also of mixtures, particularly hydrocarbons mixtures. The following rules are frequently used to obtain the parameters *a* and *b* for binary systems:

$$a = X_A^2 a_A + X_B^2 a_B + 2X_A X_B a_{AB}$$

and:

$$b = X_A b_A + X_B b_B \quad \text{…….. (5)}$$

where:

$$a_{AB} = (a_A a_B)^{0.5}(1 - L_{AB})$$

a_{AB} is the interaction constant for the two components A & B. This quantity depends upon the Redlich-Kwong parameters a_A & a_B for the pure components A and B and also on L_{AB} the interaction constant. When phase equilibrium in binary systems using the Redlich-Kwong equation**,** it is necessary to calculate the fugacity of each component present in each phase.

For equilibrium between two phases the fugacity of any component present in the phases should be the same in each phase. The fugacities are calculated from the Redlich-Kwong equation and phase compositions are found by trial and error such that these equations are satisfied at given temperature and pressure .The equation used for calculating the fugacity of a component (A) in a binary system from the (R.K) equation is :

$$In(\frac{f_{AL}}{X_A p}) = In(\frac{RT}{(V-b)p}) + \frac{b_A}{(V-b)} - \frac{ab_A}{RT^{1.5}} \left(\frac{1}{b(V+b)} + \frac{1}{b2}\ln\frac{v}{(V+b)}\right) + \frac{2(X_A a_A + X_B a_{AB})}{RT^{1.5} b} In(\frac{V}{(V+b)}) \quad \text{.....} \quad \textbf{(6)}$$

where

f_{AL} : is the fugacity of component (A) in the given phase.

X_A : is the mole fraction of component (**A)** in the given phase at temperature T(ºK) and pressure P atm., ***V*** is the molar volume.

$a_A b_A$: are Redlich-Kwong constants for component A.

$a_B b_B$: are Redlich-Kwong constants for component B.

a_{AB} : The interaction Redlich-Kwong constant of the two component A and B.

Experimental

Solubilities were predicted as functions of temperature using The Redlich-Kwong equation with a constant value for the interaction parameter L_{AB}. The value of A and B for the components were calculated from equations (3) and (4), and were taken to be independent of temperature. The values used are given in table (1).

The values of (A) and (B) for the mixtures were calculated from equation (4).

The value for L_{AB} was chosen to give an exact fit to the solubility at the temperature shown with on asterisk in table (2). This temperature at 298.15 k except for solvents which were solid at this temperature .

The mole fraction solubility of CO_2 in ethyl benzene was measured by King *et al* (1983), at normal pressure and over temperature range 296.15-333.15 K.

The interaction constant L_{AB} Was determined by fitting the mole fraction of solubility of CO_2 in the solvents and of N_2 In *n*-Hexadecane by using Redlich-Kwong equation of state. The relationship of interaction constant is used in the calculations of phase behavior. The results obtained were compared with experimental data .it gives good representation of phase equilibrium.

Results & Discussion:

The Solubility of CO_2 in the non-volatile Solvents of *n*-Hexadecane, Diphenyl methane, Diphenyl ethane, Ethyl benzene and of N_2 in n- Hexadecane, at temperature range 298.15-358.15 ºK at a partial pressure of one atmosphere were experimentally measured by falling-film flow technique Kassim, D. M. (1981) .

These data are summarized in table (2). It is seen the solubility of CO_2 decrease as temperature increase in most cases, thought in case of N_2 /*n*-Hexadecane the reverse is true. The effect is probably related to the decrease in solvent density which occurs as the temperature rises.

In case the system N_2/*n*-Hexadecane of law solubility this effect due to counter balance the increase tendency for solute molecules to "escape" from the solvent arising from their increase Kinetic energy.

The values of L_{AB} are evaluated by fitting equation (5) against the mole fraction solubility of CO_2 in each solvents and of N_2 in n-Hexadecane also, as presented in table (2). The (*) L_{AB} fitted at temperature shown with asterisk, using a suitable computer program at each temperature.

Table(1)
The value of A and B for the components were calculated from equations (3) and (4), and were taken to be independent of temperature.

Solvents, Gases	**A** $(atm)(dm^3/mol)^2 (k^{1/2})$	**B** $(dm^3)/mol$
n-Hexadecane	2867.96	0.366181
Diphenyl ethane	1675.75	0.182663
Diphenyl methane	1681.60	0.194305
Ethyl benzene	765.15	0123261
Carbon dioxide	63.77	0.029686
Nitrogen	15.38	0.026801

Table (2)

Prediction of the mole fraction solubility of CO_2 and N_2 at partial pressure of one atmosphere from the Redlich-Kwong equation of state:

System	T(°K)	$X^1_{exp}\times10^4$	$X^1_{R.K}\times10^4$	L_{AB}
CO_2/ C_8H_{10}	*298.15	71.5	71.5	0.22
	303.15	68.7	68.9	
	301.15	63.0	64.4	
	333.15	55.3	57.5	
CO_2/ $C_{13}H_{12}$	*303.15	79.2	79.2	0.20
	313.15	70.9	73.1	
	323.15	62.6	68.2	
	333.15	57.7	64.0	
	343.15	53.3	60.4	
	353.15	49.8	57.4	
CO_2/ $C_{14}H_{14}$	*333.15	76.1	76.1	0.14
	338.15	70.9	73.6	
	343.15	67.3	71.0	
	353.15	59.1	66.6	
	358.15	55.3	64.6	
CO_2/ $C_{16}H_{34}$	*299.15	139.4	139.4	0.19
	303.15	129.9	133.5	
	313.15	120.2	124.5	
	323.15	108.0	117.0	
	333.15	100.0	110.7	
	343.15	94.0	105.3	
	353.15	87.6	100.7	
N_2 / $C_{16}H_{34}$	*298.15	12.5	12.4	0.80
	303.15	12.7	12.7	
	313.15	13.2	13.5	
	333.15	14.0	14.9	
	343.15	14.2	15.6	
	353.15	14.2	-	

*L_{AB} Fitted a temperature shown with asterisk

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