Measurement of High Pressure Phase Equilibria Behaviors of Alkylaluminum/Alkane Systems by Variable Volume Cell[1]

G.B. Lim[2], J. H. Ryu[3], S. H. Kim[3], M. J. Noh[3] and K. -P. Yoo[3,4]

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[2] Department of Chemical Engineering, The University of Suwon, Suwon C.P.O.Box 77, Suwon, Korea

[3] Department of Chemical Engineering, Sogang University, C.P.O. Box 1142, Seoul, Korea.

[4] To whom correspondence should be addressed

ABSTRACT

High pressure phase equilibria of ethane- and *n*-hexane-alkylaluminum systems were measured by a variable volume view cell at 373.15~413.15 K and pressures up to 30 MPa. Feeds were injected into the cell by a syringe pump, and the phase behavior was measured by a computerized boroscope. Error ranges of measured temperature and pressure were within ±0.1 K and ±0.03 MPa, respectively. Tested alkylaluminum species were triethylaluminum, tri-*n*-butylaluminum and tri-*n*-hexyl-aluminum. Measured data were modeled using the Peng-Robinson EOS and a recently developed EOS based on lattice-hole theory by one of the present authors.

KEY WORDS: Experimental method, variable volume cell, vapor-liquid equilibria, alkylaluminum/alkane systems

1. INTRODUCTION

Since the industrial importance of alkylaluminums was demonstrated by Karl Ziegler in 1960s, active research has been focused on the direct synthesis of alkylaluminums by reacting metallic aluminum, hydrogen and olefins[1]. Recently, attention is being placed on the use of alkylaluminums since they are widely used as reaction media for the ethylene addition reaction, olefin substitution reaction, and production of alkoxide, etc[2].

Unfortunately, reliable phase equilibrium data between alkene(i.e., ethylene)/ alkylaluminum and alkane/alkylaluminum systems are extremely scarce due to their complex natures. Recently, vapor-liquid equilibria for triethylaluminum (TEAL), tri-*n*-butylaluminum (TnBAL) and tri-*n*-hexyl-aluminum(TnHAL) with ethane, using a flow-type apparatus were reported in the literature[2,3].

In the present work, further tests on the phase behavior of alkyl-aluminums with n-hexane as well as ethane were conducted using a synthetic-type variable volume view cell. Systems tested are triethylaluminum, tri-*n*-butylaluminum, and tri-*n*-hexylaluminum with ethane and *n*-hexane as solvents.

2. EXPERIMENTAL

2.1. Apparatus

The schematic diagram of the apparatus used is shown in Fig. 1. The equipment is basically similar to the one developed by Hasch and coworkers[4]. The essential component is a variable-volume view cell(Nitronic 50®, Armco Corp., 6.40 cm OD $\times$ 1.60 cm ID, $\sim$30 cm^3 working volume, fitted with a 1.90 cm OD). Inside the cell, a piston(1.60 cm OD $\times$ 2.56 cm L) and magnetic stirrer were installed. The position of

the piston was controlled by a hand pump(NOVA Co., model 555-0202-1). Solvent was transferred into the cell using a syringe pump (ISCO Co., model 260D) with associated error ranges of ±0.02g at 323.15K and 14.7 MPa. Visual determination of an equilibrium state and phase transition was conducted using a camera equipped with a boroscope(Olympus Co., model F100-024-000-55), video monitor, and a light source.

2.2. Experimental Procedure

Since alkylaluminums are apt to explosively react upon contact with oxygen or water, they were transferred into the cell using an air-tight syringe (Hamilton Co., model 81620) with a nitrogen purge line. After the cell was filled with a known amount of solute and solvent, the cell was pressurized until the mixture become a homogeneous single phase, and was maintained at least for 30 min or more until it reached thermal equilibrium. The depressurization rate was maintained at 0.03 bar/sec until a second phase emerged[5].

Pressure inside the cell and outside the piston was controlled and measured by a pressure transducer (ISI Co., model 0163-5.0CB) and Heise gauge(Dresser Inc., model CM-53920). The system temperature was maintained within ±0.1K and measured by a digital multimeter with platinum resistance sensor.

A bubble point was determined as the condition at which a small vapor volume appeared in the cell as the pressure was lowered. The liquid concentration was determined from the amount of material loaded in the cell with a negligible amount transferred to vapor bubbles. The critical point of a mixture was defined as the pressure and temperature at which a critical opalescence was observed for a slight change by either pressure or temperature.

3. DATA CORRELATION

Experimental data were illustratively correlated by a lattice EOS proposed recently by the present authors[6]and the Peng-Robinson EOS[7]. The lattice EOS is given by:

$$P = \frac{1}{\beta V_h}\left\{\frac{z}{2}\ln\left[1+\left(\frac{q_M}{r_M}-1\right)\rho\right]-\ln(1-\rho)+\frac{z}{2}\sum_{i=1}^{c}\theta_i\left(\frac{\tau_{0i}}{\sum_{k=0}^{c}\theta_k\tau_{ki}}-1\right)\right\} \quad (1)$$

$$\tau_{ji} = \exp\left[\beta\left(\varepsilon_{ji}-\varepsilon_{ii}\right)\right]; \quad (2)$$

where β =1/kT, $q_M = \Sigma x_i q_i$, $r_M = \Sigma x_i r_i$. q_i and r_i are the surface area parameter and segment number and are related by $zq_i = (z-2)r_i + 2$. ρ is the system density. z is the coordination number fixed by 10; and V_H is the lattice cell volume which is equal to 9.75 cm^3mol^{-1}. Also, we define the characteristic volume $V_i^* = N_A V_H r_i$, where N_A is Avogadro's number. Therefore, the molar volume $V = V_i^* / \rho$. If we set i and j equal to 1, Eq.(1) becomes specific for pure fluids.

For a pure fluid, we are required to determine the two independent molecular parameter, r_i and ε_{ii}. These parameters are determined by vapor pressure, saturated volume and pVT data[2,3]

The parameters determined at each isotherm were fitted to the following empirical correlation for convenient use in practice:

$$r_i = a_i + b_i\left(T-T_0\right)+c_i\left(T\ln\frac{T_0}{T}+T-T_0\right) \quad (3)$$

$$\varepsilon_{ii}/k = w_{ii} + h_{ii}\left(T-T_0\right)+d_{ii}\left(T\ln\frac{T_0}{T}+T-T_0\right) \quad (4)$$

When an EOS is used to calculate vapor-liquid equilibria, the cross interaction energy between species i and j is assumed by:

$$\epsilon_{ij} = \left(\epsilon_{ii}\epsilon_{jj}\right)^{1/2}\left(1-\lambda_{ij}\right); \qquad (5)$$

where λ_{ij} is the binary interaction parameter calculated from the data.

4. RESULTS AND DISCUSSION

Utilizing a variable-volume cell(Fig. 1), phase equilibrium pressure was measured at three isotherms(i.e., 373.15, 393.15, and 413.15 K) and compositions. For each condition, experiments were repeated three times and an arithematic mean pressure was calculated. Data are summarized in Table ¥ .°

Illustratively, data for ethane/alkylaluminum systems were modeled using the Peng-Robinson EOS and the lattice EOS. For the lattice EOS, the values of coefficients defined by Eq. (3) and (4) were estimated based on existing pure properties data[2,3] and they are summarized in Table ¥ ± For both EOSs, the same temperature-independent binary interaction parameter, λ_{ij} was employed.

In Figs. 2-4, experiemental and calculated P-T loci were compared for ethane/TEAL, ethane/TnBAL, and ethane/TnHAL, respectively. Since alkyl-aluminums tend to show complicated behavior of association[1-3], phase equilibria behavior of mixtures containing one of these substances remain difficult to model. In Fig. 2, results modeled using both EOSs are shown. As one might imagine, correlated results were not satisfactory. Instead, it appears that the classical EOSs only can be used for the purpose of qualitative estimation of phase equilibria for ethane/alkylaluminum systems.

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Table I. Measured P-T-x data for alkane/alkylaluminum systems

Mole fraction	Pressure [MPa]		
x_i	373.15 K	393.15 K	413.15 K
(1) ethane/triethylaluminum system			
0.3210	6.58	7.30	7.87
0.4400	8.32	9.32	10.97
0.7610	12.51	14.37	15.31
0.7617	12.73	14.26	15.28
0.8081	12.80	14.19	15.18
0.8388	12.67	14.04	14.80
0.8826	12.39	13.52	14.38
0.8971	11.98	12.81	13.60
(2) ethane /tri-*n*-butyl aluminum system			
0.4256	7.54	8.99	10.00
0.7295	12.68	13.95	15.20
0.7961	12.96	14.46	15.66
0.8919	13.46	14.85	15.77
0.9148	12.91	14.58	15.08
(3) ethane/tri-*n*-hexylaluminum system			
0.5640	12.04	13.00	13.75
0.7799	15.06	16.23	16.99
0.8408	15.64	17.18	18.35
0.9036	16.11	17.85	19.21
0.9278	15.93	17.59	18.97
(4) *n*-hexane/triethylaluminum system			
0.4636	2.00	2.08	2.38
0.6394	1.86	1.90	2.18
0.6985	1.73	1.82	1.95
0.8470	1.32	1.52	1.66
0.9500	0.99	1.24	1.37
(5) *n*-hexane/tri-*n*-butylaluminum system			
0.4902	3.02	3.14	3.24
0.6318	2.71	2.79	2.85
0.7659	1.95	1.98	2.08
0.8113	1.56	1.67	1.85
0.8983	0.86	0.97	1.18
(6) *n*-hexane/tri-*n*-hexylaluminum system			
0.3508	3.46	3.69	4.00
0.5596	3.71	4.01	4.32
0.7650	2.95	3.25	3.70
0.8510	2.36	2.51	2.94
0.8900	1.36	1.58	1.87

Table II. Estimated values of coeffiencts in Eq. (3) and (4).

	E_a	E_b	E_c	V_a	V_b	V_c
Ethane	75.30597	-0.00782	-0.10958	50.00875	0.00851	0.02579
TEAL	122.77029	-0.06180	-0.44600	98.77651	0.29762	1.49027
TnBAL	121.31277	-0.04268	-0.15832	121.88644	0.01734	-0.18096
TnHAL	125.69364	-0.05844	0.05857	149.01560	-0.46339	-3.69929

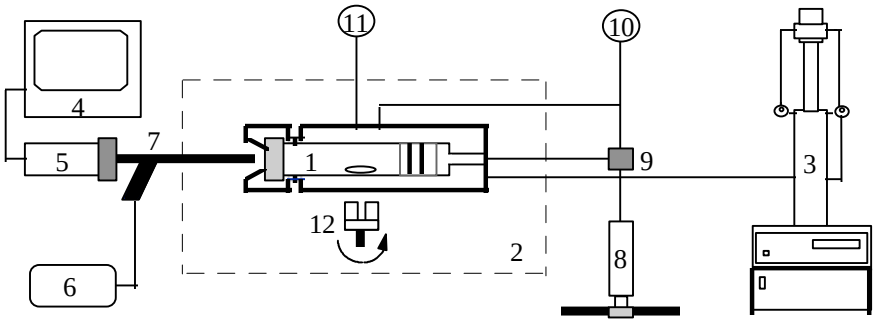
FIGURE CAPTIONS

Fig. 1. Schematic diagram of a synthetic equilibrium cell used in this study.

Fig. 2. Measured and calculated P-T-x data for the ethane/triethylaluminum system.

Fig. 3. Measured and calculated P-T-x data for the ethane/tri-*n*-butylaluminum system.

Fig. 4. Measured and calculated P-T-x data for the ethane/tri-*n*-hexylaluminum system .



1: Equilibrium Cell
2: Air Bath
3: Syringe Pump
4: Video Monitor
5: Camera
6: Light Source
7: Boroscope
8: Pressure Control Device
9: Pressure Transducer
10: Pressure Indicator
11: Temperature Indicator
12: Magnetic Stirrer

Fig. 1. Schematic diagram of a synthetic equilibrium cell used in this study.

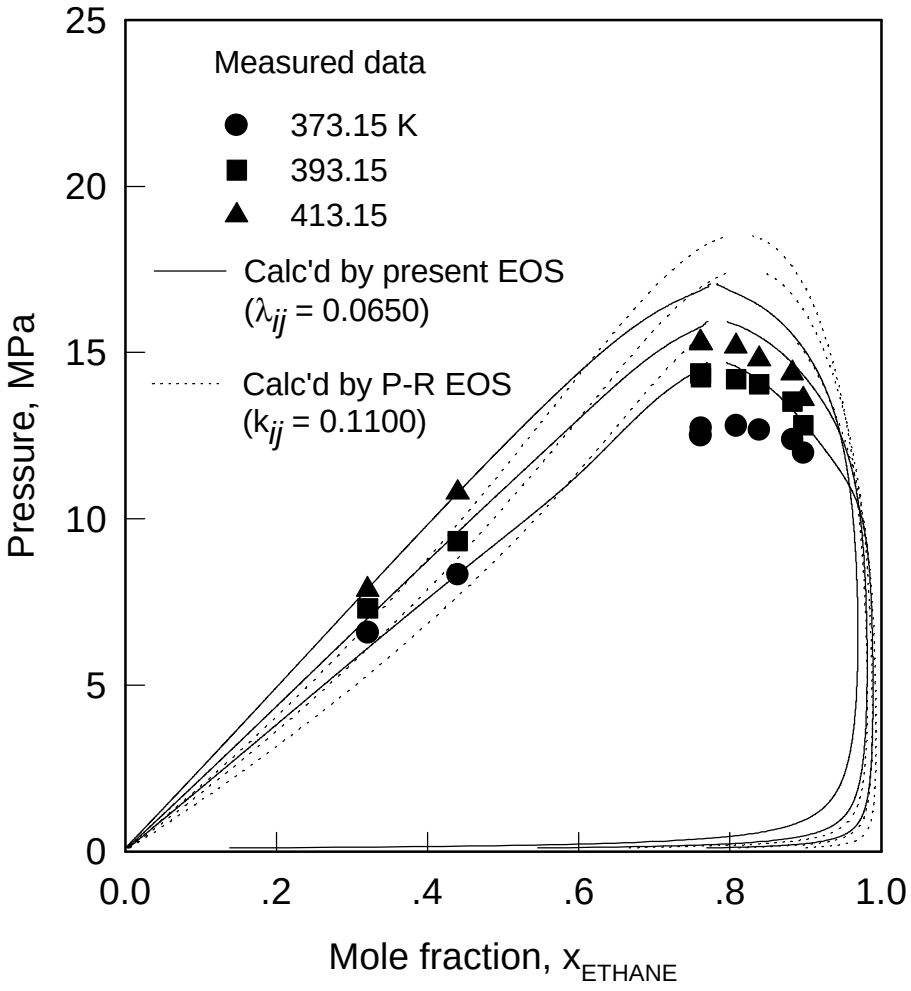


Fig. 2. Measured and calculated P-T-x data for the ethane/triethylaluminum system

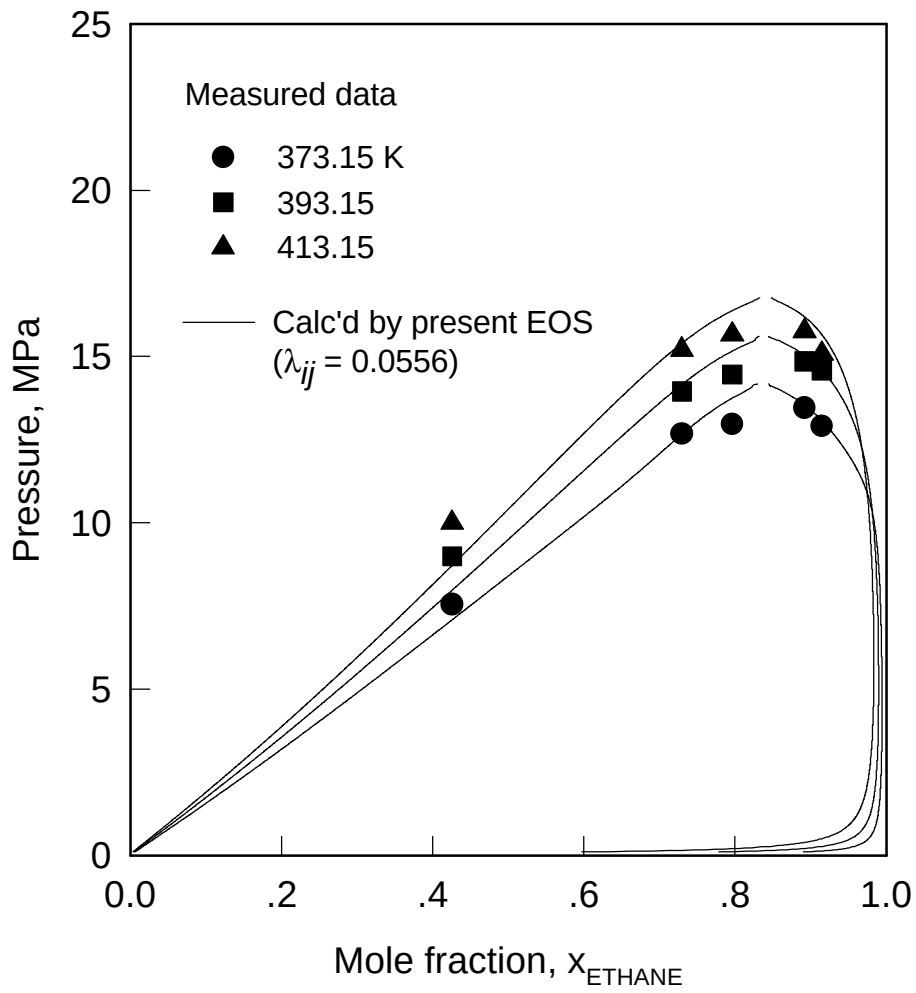


Fig. 3. Measured and calculated P-T-x data for the ethane/tri-*n*-butylaluminum system

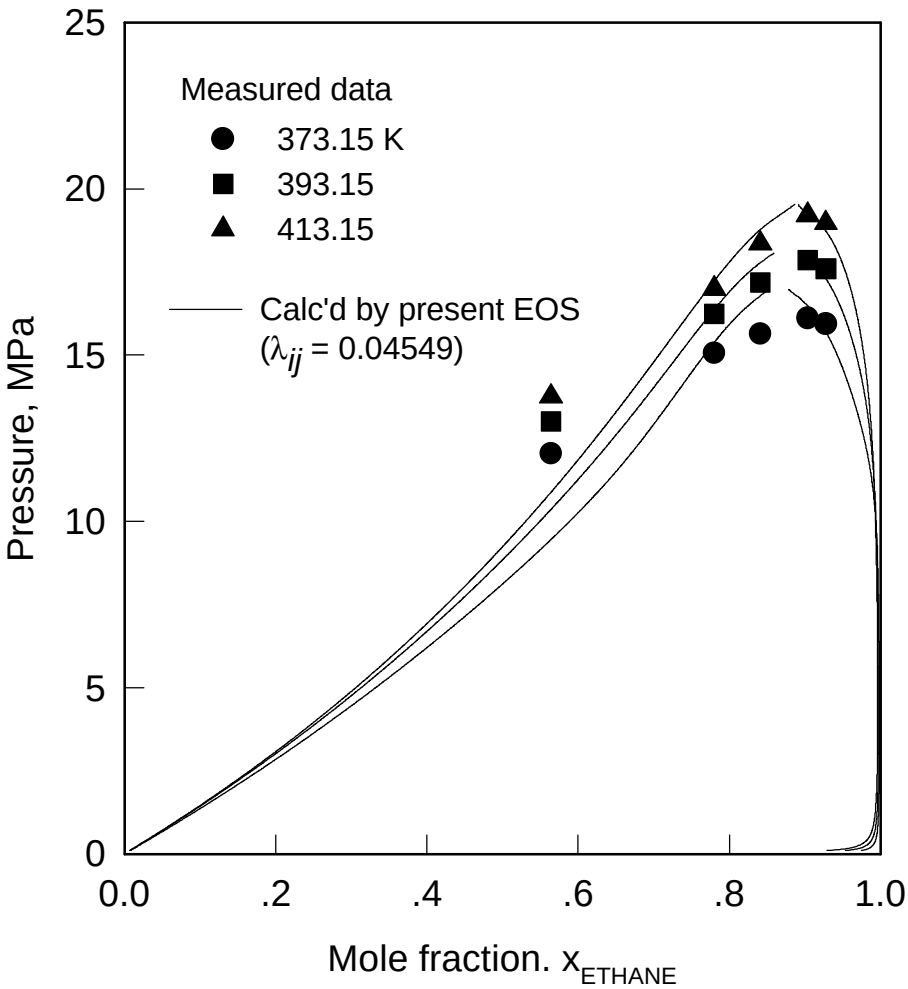


Fig. 4. Measured and calculated P-T-x data for the ethane/tri-*n*- hexylaluminum system