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VAPOUR-LIQUID EQUILIBRIA OF CYCLOHEXANE-DIISOPROPYL ETHER SYSTEM

S. RAMACHANDRAN¹, A. BARADARAJAN AND M. SATYANARAYANA*
Department of Chemical Engineering, Indian Institute of Technology, Madras, India

The experimental set-up used was a recirculatory type of equilibrium still described elsewhere³. Vapour pressures and temperature data for cyclohexane and diisopropyl ether were taken from the literature^{4,5}. The data were plotted for graphical interpolation.

Both specific gravity and refractive index were used as check measurements for the analysis of mixtures. The specific gravity-refractive index composition data were plotted for graphical interpolation.

Results

Vapour-liquid equilibrium data obtained at atmospheric pressure are presented in **Table 1**.

Correlations

The activity coefficients of diisopropyl ether were calculated from the relation

$$\gamma_1 = \frac{\pi y_1}{p_1 x_1} \quad (1)$$

where π is the total pressure of the system, p_1 is the vapour pressure of pure diisopropyl ether; x_1 , the composition of liquid in terms of mole fraction of diisopropyl ether; and y_1 , the composition of vapour in equilibrium with liquid of composition x_1 . The activity coefficients were corrected for non-ideality in vapour phase using the method of Mertes and Colburn⁶ as follows:

$$\gamma_1 = \frac{\pi y_1}{p_1 x_1} \exp \frac{(p_1 - \pi)(v_1 - \beta_1)}{RT} \quad (2)$$

where v_1 is the molal volume of liquid diisopropyl ether and β_1 the second virial coefficient, $RT/p(z-1)$. The activity coefficient data are presented in **Fig. 1**.

The activity coefficients were correlated by the van Laar equations⁷

$$T \ln \gamma_1 = \frac{B'}{\{1 + A'(x_1/x_2)\}^2} \quad (3)$$

$$T \ln \gamma_2 = \frac{A'B'}{\{A' + (x_2/x_1)\}^2} \quad (4)$$

The constants A' and B' in Eqs. (3) and (4) were evaluated from the plots of $1/(T \ln \gamma_1)^{1/2}$ versus x_1/x_2 and $1/(T \ln \gamma_2)^{1/2}$ versus x_2/x_1 .

Using these correlations, the x_1 versus y_1 data were calculated. The experimental and calculated values

Table 1 Vapour-liquid equilibrium data for diisopropyl ether-cyclohexane system at 760 mm Hg

Van Laar constants: $A' = 0.3048$; $B' = 55.68$

Wilson parameters: $A_{12} = -0.0164$, $A_{21} = 1.3774$

t [°C]	x_1	y_1	y_1 cal(van)	y_1 cal(W11)
80.75	0.0000	0.0000	0.0000	—
79.20	0.0450	0.0600	0.0834	0.0756
78.80	0.0650	0.0850	0.1177	0.0972
77.10	0.1450	0.1850	0.2416	0.1569
76.00	0.2000	0.2550	0.3178	0.2420
75.00	0.2700	0.3300	0.4033	0.3500
74.20	0.3300	0.3850	0.4708	0.3922
73.00	0.4350	0.4900	0.5718	0.5128
72.50	0.4800	0.5300	0.6113	0.5519
71.30	0.6050	0.6600	0.7119	0.6626
69.60	0.8250	0.8600	0.8621	0.8464
69.20	0.8700	0.9000	0.8927	0.8871
68.50	1.0000	1.0000	1.0000	—

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¹ Scientist, National Chemical Laboratory, Poona, India

are presented in Table 1. The values of A' and B' are given in Table 1. Wilson¹⁾ parameters for this system were evaluated by the non-linear least square method with the minimization of the following function:

$$S = \sum_{i=1}^N \gamma_i^2$$

where

$$\gamma_i = (Q_{\text{exp}} - Q_{\text{ca}})_i = \{(x_2 \ln \gamma_1 + x_2 \ln \gamma_2) - [-x_1 \ln(x_1 + A_{12}x_2) - x_2 \ln(A_{21}x_1 + x_2)]\}_i$$

Relaxation technique was employed to avoid the divergence of the series. The calculations were made with the help of an IBM 1130 computer. Wilson parameters and correlations are also shown in Table 1. The excess free energy and the activity coefficients may be expressed by the Redlich-Kister equation for binary system as

$$Q = \frac{\Delta G^E}{2.303RT} = x_1x_2[B + C(x_1 - x_2) + \dots] \quad (5)$$

$$\log \gamma_1 = x_2^2[B + C(3x_1 - x_2) + \dots] \quad (6)$$

$$\log \gamma_2 = x_1^2[B + C(x_1 - 3x_2) + \dots] \quad (7)$$

The heat of mixing data may be represented by an analogous equation:

$$\Delta H_{\text{mix}} = x_1x_2[b + c(x_1 - x_2) + \dots] \quad (8)$$

Since

$$\Delta H_{\text{mix}} = \frac{\partial(\Delta G^E/T)}{\partial(1/T)} = 2.303R x_1x_2 \times \left[\frac{\partial B}{\partial(1/T)} + (x_1 - x_2) \frac{\partial C}{\partial(1/T)} + \dots \right] \quad (9)$$

The following equations can be written:

$$b = 2.303R \frac{dB}{d(1/T)} \quad (10)$$

$$c = 2.303R \frac{dC}{d(1/T)} \quad (11)$$

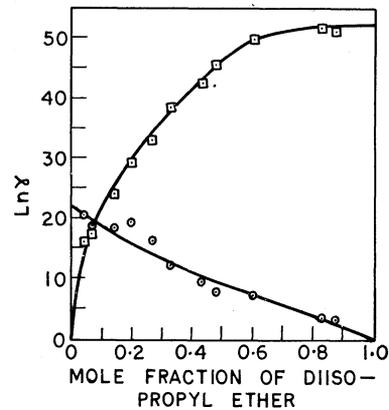
Heat of Mixing Term

The values of the Redlich-Kister constants B and C were determined at different temperatures using Eqs. (6) and (7). From the plots of B vs. $1/T$ and C vs. $1/T$, values of $dB/d(1/T)$ and $dC/d(1/T)$ were obtained and used to determine constants b and c at any specific temperature from Eqs. (10) and (11). Heat of mixing for any particular liquid composition was determined using Eq. (8) and using values of b and c at the boiling point of this solution.

The isobaric form of the Gibbs-Duhem equation for a binary mixture can be written as follows, as shown by Ibl and Dodge³⁾.

$$x_1 \frac{d(\ln \gamma_1)}{dx_1} + x_2 \frac{d(\ln \gamma_2)}{dx_1} = -\frac{\Delta H}{RT^2} \left(\frac{\partial T}{\partial x_1} \right) \quad (12)$$

$$\int_{Q_1}^{Q_2} dQ = \int_{x_1=0}^{x_1=1} \ln \left(\frac{\gamma_1}{\gamma_2} \right) dx_1 - \int_{x_1=0}^{x_1=1} \frac{\Delta H}{RT^2} \left(\frac{\partial T}{\partial x_1} \right) dx_1 = 0 \quad (13)$$



○—○ $\ln \gamma_1$ vs. x_1 □—□ $\ln \gamma_2$ vs. x_2

Fig. 1 Activity coefficient-composition plot of cyclohexane-Diisopropyl ether system at 760 mmHg

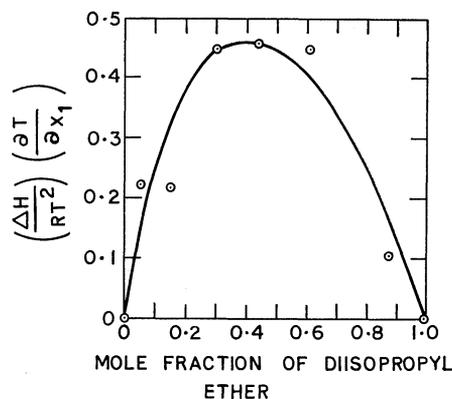


Fig. 2 Heat of mixing function

Table 2 Heat of mixing data

t [°C]	B	C	ΔH	$\left(\frac{\partial T}{\partial x_1}\right)$	$\left(\frac{\Delta H}{RT^2}\right) \left(\frac{\partial T}{\partial x_1}\right)$
79.20	-13.75	-16.89	10.75	-21.29	-0.2219
77.10	-0.93	-2.47	13.20	-16.36	-0.2118
75.00	+0.67	-0.68	35.26	-12.71	-0.4450
73.00	+0.98	-0.42	45.89	-9.90	-0.4563
71.30	+1.20	-0.19	55.28	-8.00	-0.4485
69.20	+1.70	+0.25	28.98	-3.48	-0.1036

The values of $\partial T/\partial x_1$ were obtained from an experimental plot of T vs. x_1 . The quantity $\Delta H/RT^2$ ($\partial T/\partial x_1$) was then computed for various values of x_1 and its values are shown in Table 2 and Fig. 2.

Conclusion

Wilson equations correlate the experimental vapour-liquid equilibrium data better than the van Laar equations.

Nomenclature

- A' = van Laar constant in Eqs. (3) and (4)
- B = Redlich-Kister constant in Eqs. (6) and (7)
- B' = van Laar constant in Eqs. (3) and (4)
- b = Redlich-Kister constant defined by Eq. (10)
- C = Redlich-Kister constant in Eqs. (6) and (7)

c	= Redlich-Kister constant defined by Eq. (11)
G	= free energy
H	= heat of mixing
p	= vapour pressure
R	= gas constant
S	= a function defined by $S = \sum_{i=1}^N \gamma_i^2$
T	= absolute temperature
v	= molar volume of liquid
x	= mole fraction in liquid phase
y	= mole fraction in vapour phase
γ	= activity coefficient
π	= total pressure of the system

<Subscripts>

1	= diisopropyl ether
2	= cyclohexane
exp.	= experimental
cal.	= calculated
i	= i th component

<Superscript>

E	= excess
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VAPOR-LIQUID EQUILIBRIUM OF MINOR COMPONENT — ACETONE-METHYL ACETATE SYSTEM CONTAINING A MINUTE AMOUNT OF CHLOROFORM —

ATSUSHI IKARI*, KIMIKO MURATA AND SHIGERU MATSUSHITA¹
Department of Chemical Engineering, Kagoshima University, Kagoshima, 890

The vapor-liquid equilibrium of acetone-methyl acetate system containing a minute amount of chloroform was measured at 1 atm. Experiments were carried out in two concentration ranges with respect to the minor component, chloroform.

The data and the activity coefficients are presented in this paper.

Experiment

An Othmer-type equilibrium still was used. About 230 ml solution was charged into the still. After operation of the still for 5 to 6 hr., samples of the liquid phase and the condensed-vapor phase were drawn for analysis.

The analytical procedure is as follows.

a) The density of samples is measured by an Ostwald pycnometer at 20°C. The uncorrected concentration of methyl acetate (M') is obtained by the density line of acetone-methyl acetate system, which has been prepared previously.

b) When the mole fraction of the minor component in the liquid phase was in the smaller range (from

0.000171 to 0.000589), the concentration of the component was measured by colorimetry.

The concentration of methyl acetate in a sample is adjusted to 50 vol% by adding a few milliliters of acetone or methyl acetate, which is calculated from the uncorrected concentration obtained in a). After that, 5 ml of the solution is taken to be colored by Cole's method¹⁾. The absorbancy at 530 m μ is measured with a photoelectric colorimeter, and the concentration of chloroform is obtained from the calibration curve, which has been prepared previously.

A Spectronic 20 (Shimadzu) was used.

c) When the mole fraction of the minor component in the liquid phase was in the larger range (from 0.00218 to 0.00335), the concentration of the component was measured on a gas chromatograph (Shimadzu GC-3BT) with a thermal-conductivity detector. The column was packed with 25% polyethylene glycol 6000 on Shimalite support.

An internal standard method is used with *n*-butyl alcohol as the reference compound.

d) From the concentration of chloroform (C), the corrected concentration of methyl acetate (M) is ob-

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¹ Shinko-Pfaudler Co., Ltd., Kobe