

## DETERMINATION AND CORRELATION OF LLE AND SLE DATA FOR THE SYSTEM ANILINE+CYCLOHEXANE

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(Received 19 May 1997 • accepted 20 June 1997)

**Abstract** – A newly developed laser light scattering technique was used for the determination of mutual solubilities in the aniline+cyclohexane system at moderate pressures. The liquid-liquid equilibria (LLE) were measured from the region of solid-liquid equilibria (SLE) to the upper critical solution temperature. Freezing points in this system were determined by a cooling curve method. The solubility data were correlated with the NRTL equation.

**Key words:** Liquid-Liquid Equilibria, Cloud Point, Laser Scattering Technique, Solid-Liquid Equilibria, Aniline-Cyclohexane System

### INTRODUCTION

Reliable phase equilibrium data are essential for development and design of chemical processes. For systems with limited miscibility, phase equilibrium data measured in different laboratories often show discrepancies. In case of LLE and SLE, no thermodynamic analysis is presently available to establish the accuracy of experimental data. For partially miscible systems, there is still a need to test and improve experimental techniques for determining phase equilibria. Some of our attempts to develop such a technique have already been published [Ochi et al., 1993; Ochi et al., 1996]. The present work is a continuation of our previous studies.

### EXPERIMENTAL SECTION

#### 1. Measurement of Cloud Points

A schematic diagram of the apparatus used in this work is shown in Fig. 1. The equipment consists of an equilibrium vessel with a capacity of about 120 cm<sup>3</sup>, an optical system and a data integrating system. The equilibrium cell (Taiatsu Scientific Glass Co. Ltd.) is made of pressure glass which can withstand 15 bars, covered by a double jacket for cooling or heating media and evacuation. This temperature controlling system facilitates the measurement of the cloud point at low temperature region and prevents a light sensor from temperature effects. The optical system consists of a light source (a He-Ne laser, Model GLG 5090 from NEC Co.; Max 1 mW; CW, 632.8 nm) and a light sensor (selenium photocell). The light sensor is placed aside of straight way of light beams. In such installation, the weak scattered light appearing in formation or disappearance of turbidity can be effectively detected.

For our measurements, a mixture of a known com-

position with a volume of about 100 cm<sup>3</sup> was charged into the equilibrium cell. The composition of the mixture was determined by weighting the pure components on a Mettler digital balance prior to the mixing. Mixing of the cell was started and circulation of heating or cooling media was followed. At temperature above 283 K, water was used as the heating/cooling medium. Below 283 K, the system temperature was controlled by circulating ethanol.

The rate of the temperature change in the vicinity of the cloud point was controlled within 0.1 K/min so that the cloud point temperature in heating and cooling branches agreed within 0.1 K. The change in light intensity with temperature was monitored by computer via a digital multimeter.

An experimentally determined intensity of light scattering

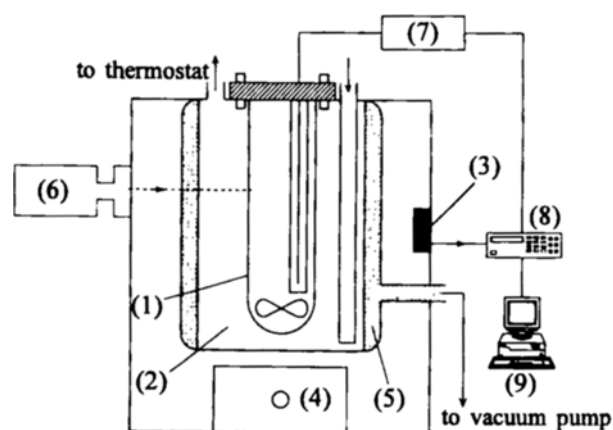


Fig. 1. A schematic diagram of apparatus for measuring mutual solubility curve.

- |                                      |                       |
|--------------------------------------|-----------------------|
| 1. Equilibrium cell (pressure glass) | 6. He-Ne laser        |
| 2. Temperature bath                  | 7. Thermometer        |
| 3. Light sensor (selenium cell)      | 8. Digital multimeter |
| 4. Magnetic stirrer                  | 9. Personal computer  |
| 5. Adiabatic jacket                  |                       |

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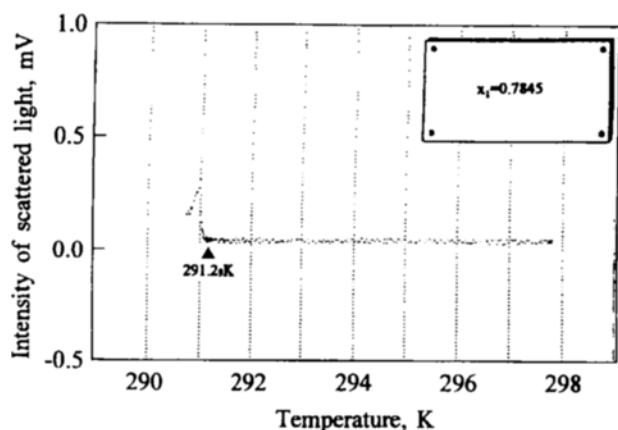


Fig. 2. An illustration of the intensity of the intensity of scattered light vs the temperature of solution for aniline(1)+cyclohexane(2) monitored by a computer.

was illustrated in Fig. 2. In the vicinity of the cloud point, the turbidity of the solution sharply decreased and this was reflected by the lowering of the intensity of the light scattering. The subsequent horizontal portion of the plot indicates an uniphase region where the solution is transparent. The cloud point determine at turning point from a turbid solution to a clear uniphase region is marked with the sign  $\blacktriangle$  in the figure. In this work, the detection of the scattered light during formation or disappearance of turbidity for a mixture was repeated to check the effect of viscosity of aniline on the reproducibility of the cloud point. The experimental cloud point temperatures depicted in the following examples were determined during the heating process.

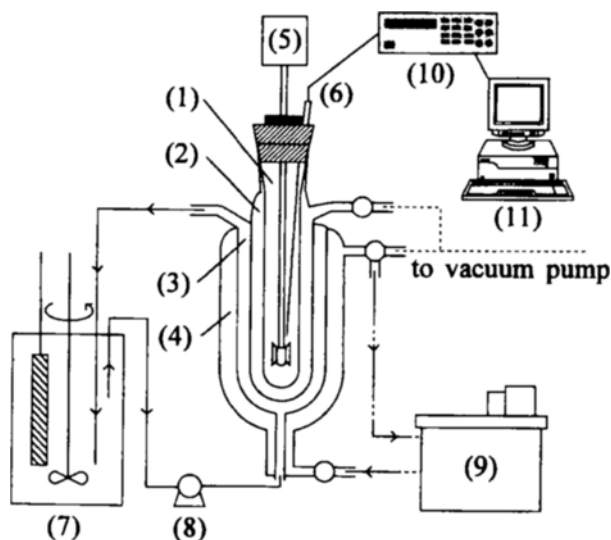


Fig. 3. A schematic diagram of apparatus for freezing point measurements.

- |                                   |                        |
|-----------------------------------|------------------------|
| 1. Equilibrium cell               | 7. Cooling media bath  |
| 2. Vacuum jacket                  | 8. Pump                |
| 3. Cooling media jacket           | 9. Heating media bath  |
| 4. Vacuum or heating media jacket | 10. Digital multimeter |
| 5. Stirrer                        | 11. Personal computer  |
| 6. Thermometer                    |                        |

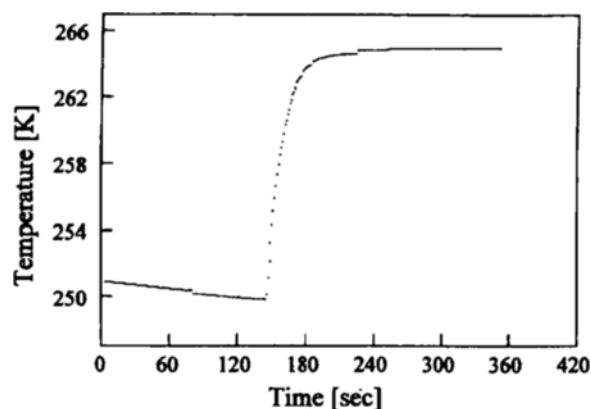


Fig. 4. Typical experimental cooling curve monitored by a computer for aniline(1)+cyclohexane(2) ( $x_1=0.9786$ ).

## 2. Measurement of Freezing Point

The apparatus for the measurement of freezing points is schematically shown in Fig. 3. The apparatus consists of an equilibrium cell with the capacity about 150 cm<sup>3</sup> covered with a triple jacket (vacuum and cooling and heating media). The combination of cooling and heating jackets significantly reduces the time requirements for the experiment. In this study, ethanol was used as the cooling medium.

About 100 cm<sup>3</sup> of a mixture of known composition was charged into the equilibrium cell. Mixing of the cell was started and circulation of cooling media was followed. Liquid temperature was monitored by a computer via a digital multimeter to obtain the cooling curve. Fig. 4 is the typical experimental cooling curve monitored by a computer. The freezing curve monitored by a computer. The freezing points were considered to be highest temperature reached after subcooling. In this study, the freezing point was determined from the horizontal branch of a cooling curve.

If the cooling proceeds too rapidly or too slowly, the meas-

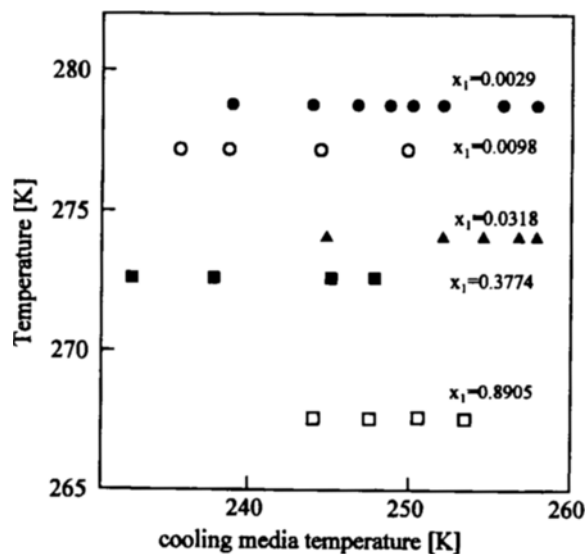


Fig. 5. Liquid mutual solubilities and freezing points for the system aniline(1)+cyclohexane(2).

- ,  $x_1$  (mole fraction of aniline)=0.0029; ○,  $x_1=0.0098$ ;  
 $\blacktriangle$ ,  $x_1=0.0318$ ;  $\blacksquare$ ,  $x_1=0.3774$ ;  $\square$ ,  $x_1=0.8905$ .

ured freezing temperatures will be different. The measurements were then repeated at several different temperatures of the cooling medium. The reproducibility of the cooling point was also reconfirmed by increasing the rotation of stirrer along with an increase in the viscosity of a mixture. Some experimental results are illustrated in Fig. 5.

### 3. Materials

Aniline and cyclohexane were supplied as special grade by Wako Pure Chemical Industries Ltd., Japan. The purities of the materials were established by gas chromatography to be better than 99.9 %.

## RESULTS AND DISCUSSION

The cloud points for the system aniline+cyclohexane have been reported by Buchner and Kleyn [1924] and the upper critical solution temperature (UCST) by Skripov and Faizullin [1989]. Discrepancy between these two sets of data is shown in Fig. 6. As the behavior of the system in the vicinity of the upper critical solution point and the low temperature range still require experimental verification, in this study the cloud points were measured in small composition increments. The experimental cloud points are listed in Table 1 compared with the literature values in Fig. 6. It can be seen that our UCS point is in excellent agreement with the point of Skripov and Faizullin. The lower limit of the liquid-liquid solubility curve was determined by measuring the freezing points. The experimental freezing points are listed in Table 2 and also shown in Fig. 6.

### DATA REDUCTION

The experimental cloud points and freezing points were simultaneously correlated by the NRTL equation [Renon and

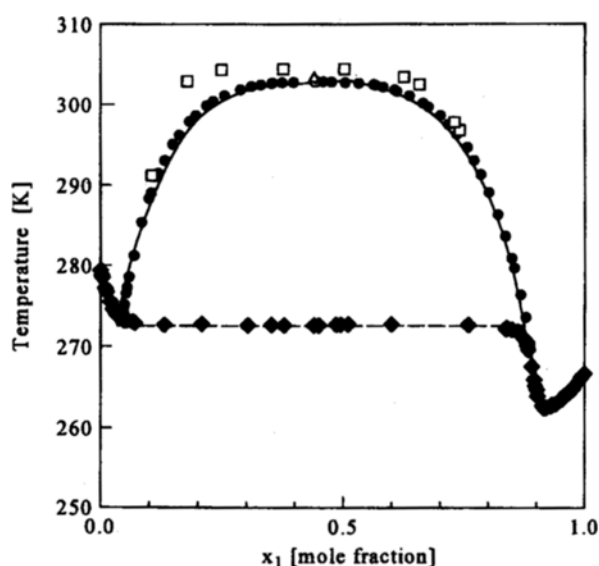


Fig. 6. Liquid mutual solubilities and freezing points for the system aniline(1)+cyclohexane(2).

●, this work (cloud point); ◆, this work (freezing point); ○, experimental upper critical solution point; □, E. H. Bucher et al.; ▲, Skripov et al.; —, correlated by NRTL equation.

Table 1. Experimental cloud point results for aniline(1)+cyclohexane(2)

$x_1^f$	T/K	$x_1^f$	T/K	$x_1^f$	T/K
0.0471	274.40	0.2548	301.12	0.6109	301.65
0.0489	275.11	0.2876	301.88	0.6369	301.08
0.0521	276.53	0.3105	302.31	0.6651	300.19
0.0545	277.30	0.3295	302.51	0.6760	299.71
0.0585	278.56	0.3522	302.72	0.7010	298.62
0.0687	281.23	0.3538	302.74	0.7169	297.48
0.0846	285.31	0.3734	302.77	0.7351	296.24
0.0991	288.32	0.3971	302.83	0.7567	294.63
0.1042	289.02	0.4425*	302.92*	0.7705	293.05
0.1181	291.43	0.4586	302.91	0.7845	291.29
0.1318	293.03	0.4756	302.86	0.8008	289.08
0.1482	295.03	0.5037	302.77	0.8200	286.27
0.1621	296.18	0.5318	302.68	0.8349	283.57
0.1829	297.84	0.5624	302.52	0.8485	280.87
0.1961	298.62	0.5662	302.45	0.8540	279.66
0.2179	299.85	0.5817	302.21	0.8669	276.33
0.2315	300.40	0.6058	301.87	0.8782	273.54

\*Mole fraction of aniline.

\*The upper critical solution point.

Prausnitz, 1968]:

$$g^E/RT = x_1x_2\{\tau_{21}\exp(-\alpha\tau_{21})/[x_1 + x_2\exp(-\alpha\tau_{21})] + \tau_{12}\exp(-\alpha\tau_{12})/[x_2 + x_1\exp(-\alpha\tau_{12})]\} \quad (1)$$

In this work  $\alpha=0.20$  was adopted for the system studied. The temperature dependence of the two parameters,  $\tau_{12}$  and  $\tau_{21}$  in Eq. (1) was expressed by the following functions:

$$\tau_{12} = \sum_{i=0}^n A_i T^i, \quad \tau_{21} = \sum_{i=0}^n B_i T^i \quad (2)$$

The coefficients of Eq. (2) were estimated by Marquardt

Table 2. Experimental freezing point results for aniline(1)+cyclohexane(2)

$x_1^f$	T/K	$x_1^f$	T/K	$x_1^f$	T/K
0.0000	279.42	0.3515	272.64	0.8954	265.93
0.0029	278.78	0.3774	272.61	0.8969	265.16
0.0038	278.53	0.4390	272.61	0.9004	264.70
0.0098	277.19	0.4489	272.62	0.9020	263.93
0.0125	276.75	0.4854	272.69	0.9125	262.72
0.0205	275.46	0.4942	272.68	0.9155	262.42
0.0264	274.60	0.5100	272.74	0.9196	262.49
0.0289	274.35	0.5996	272.73	0.9284	262.68
0.0312	274.13	0.7587	272.65	0.9312	262.81
0.0318	274.07	0.8365	272.15	0.9396	262.92
0.0328	273.94	0.8378	272.27	0.9507	263.43
0.0489	273.16	0.8495	272.06	0.9592	264.00
0.0520	273.31	0.8610	271.80	0.9656	264.26
0.0543	273.21	0.8742	270.95	0.9746	264.69
0.0660	273.01	0.8800	270.52	0.9756	264.77
0.0705	272.89	0.8804	270.11	0.9786	265.10
0.1307	272.66	0.8811	270.51	0.9914	266.05
0.2077	272.78	0.8830	269.59	0.9966	266.48
0.3026	272.60	0.8905	267.55	1.0000	266.64

\*Mole fraction of aniline.

**Table 3. Parameters of Eq. (2)**

$A_0 = 8.662946 \times 10^3$	$B_0 = -2.152324 \times 10^3$
$A_1/K^{-1} = -1.204384 \times 10^2$	$B_1/K^{-1} = 3.016214 \times 10^2$
$A_2/K^{-2} = 6.273648 \times 10^{-1}$	$B_2/K^{-2} = -1.583066$
$A_3/K^{-3} = -1.450963 \times 10^{-3}$	$B_3/K^{-3} = 3.689042 \times 10^{-3}$
$A_4/K^{-4} = -1.257102 \times 10^{-6}$	$B_4/K^{-4} = -3.220952 \times 10^{-6}$

method [Marquardt, 1963]. The following constraints were employed in the estimation:

for the upper critical solution,

$$\frac{1}{x_1 x_2} + \frac{\partial^2(g^E/RT)}{\partial x_1^2} = 0 \quad (3)$$

$$\frac{(x_1 - x_2)}{x_1^2 x_2^2} - \frac{\partial^3(g^E/RT)}{\partial x_1^3} = 0 \quad (4)$$

$$\frac{2(1 - 3x_1 x_2)}{x_1^3 x_2^3} - \frac{\partial^4(g^E/RT)}{\partial x_1^4} > 0 \quad (5)$$

for the liquid-liquid equilibria,

$$\gamma_1' x_1' = \gamma_1'' x_1'' \text{ and } \gamma_2' x_2' = \gamma_2'' x_2'' \quad (6)$$

and for the solid-liquid equilibria

$$\ln(\gamma_i x_i) = \left( \frac{T - T_i^m}{RT} \right) \left( \frac{\Delta H_i^f}{T_i^m} \right) \quad (7)$$

The estimated coefficients of Eq. (2) are given in Table 3. The results correlated by the NRTL equation are compared with the experimental values in Fig. 6. As can be seen in Fig. 6, the NRTL equation is favorably comparable with the LLE data.

### CONCLUSION

A newly developed laser scattering technique was used for the determination of LLE in aniline+cyclohexane system. The LLE data were determined from the region of SLE to the up-

per critical solution temperature. The experimental LLE and SLE data were satisfactorily correlated by the NRTL equation.

### NOMENCLATURE

- $A_i, B_i$ : constants in Eq. (2) [ $K^{-i}$ ]  
 $g^E$ : molar excess Gibbs free energy [J/mol]  
 $\Delta H_i^f$ : heat of fusion for pure component  $i$  [J/mol]  
 $R$ : gas constant [J/mol·K]  
 $T$ : temperature [K]  
 $x_i$ : mole fraction of component  $i$  in liquid [-]  
 $x_i^s, x_i^l$ : mutual solubilities [-]  
 $\alpha$ : constant in Eq. (1) [-]  
 $\tau_{ij}$ : parameter in Eq. (1) expressed by Eq. (2) [-]

### REFERENCES

- Buchner, E. H. and Kleyn, D., "Recherches sur le Systeme Cyclohexane-Aniline", *Recl. Trav. Chim. Pays-Bas*, **43**, 153 (1924).  
 Marquardt, D. W., "An Algorithm for Least-Squares Estimation of Nonlinear Parameters", *J. Soc. Ind. Appl. Math.*, **11**, 431 (1963).  
 Ochi, K., Momose, M., Kojima, K. and Lu, B. C.-Y., "Determination of Mutual Solubilities in Aniline+n-Hexane and Furfural+Cyclohexane Systems by a Laser Light Scattering Technique", *Can. J. Chem. Eng.* **71**, 982 (1993).  
 Ochi, K., Saito, T. and Kojima, K., "Measurement and Correlation of Mutual Solubilities in 2-Butanol+Water", *J. Chem. Eng. Data*, **41**, 361 (1996).  
 Renon, H. and Prausnitz, J. M., "Local Composition Thermodynamic Excess Functions for Liquid Mixture", *AIChE J.*, **14**, 135 (1968).  
 Skripov, V. P. and Faizullin, M. Z., "Thermodynamic Similarity of Phase Separating Binary Liquid Mixtures Having an Upper Critical Temperature", *J. Chem. Thermodynamics*, **21**, 687 (1989).