γ = activity coefficient, see Eq.(1)
 $\gamma' = y_i P / x_i P_i^0$
 A = binary parameter of Wilson equation
 <Subscript>
 az = refers to azeotropic point
 1 = refers to methyl acetate
 2 = refers to methanol
 3 = refers to water

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TERNARY LIQUID-LIQUID EQUILIBRIA FOR THE SYSTEMS SODIUM LIQUID AMMONIA SOLUTION AND BENZENE OR CYCLOHEXENE*

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Ternary liquid-liquid equilibrium data for the systems benzene-sodium-ammonia and cyclohexene-sodium-ammonia were measured at 20°C. A method for prediction of the mutual solubility of sparingly soluble mixtures in the ternary liquid-liquid equilibria was proposed by the application of Ishida's correlation using the data of the ternary liquid-liquid equilibria. On the basis of the above results, a point at which solid and heterogeneous liquids are in equilibrium was determined.

The manufacture of 1,4-cyclohexadiene by the reduction of benzene in sodium-liquid ammonia solution has recently attracted increasing attention by virtue of many advantages¹). To separate the products from the reactions, it is necessary in this process to know the precise equilibrium data for the systems benzene-sodium-ammonia and cyclohexene-sodium-ammonia.

The properties of alkali metal-ammonia solutions have been widely investigated from many view-points, but no study of the reduction of aromatic hydrocarbons in a sodium-liquid ammonia solution is found in the literature to the present authors' knowledge.

Although reaction of sodium with liquid ammonia yields sodium amide and hydrogen even in the absence of catalyst such as ferric oxide, the rate of reaction is so small that the influence on the variation

of the composition of this solution can be neglected⁶). However, since sodium-liquid ammonia solution reacts rapidly with 1,4-cyclohexadiene at room temperature, it was impossible to determine the phase relationships for the systems containing 1,4-cyclohexadiene.

The ternary liquid-liquid equilibria for the systems of sodium-liquid ammonia solution and benzene or cyclohexene at 20°C were determined neglecting the production of sodium amide.

Materials and Methods

Liquid ammonia used in this work was purified from the commercial product by repeating its careful distillation more than three times under pressure. Commercially available benzene was further purified by the usual method and the fraction of boiling point 80.0°~80.1°C (1 atm), melting point 5.53°C (1 atm), d_4^{20} 0.8784, n_D^{20} 1.5011 was used.

Sodium-liquid ammonia solution was prepared in a pressure glass bottle having a glass filter, as shown

* Received on February 18, 1971

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Table 1 Benzene-sodium-ammonia equilibrium compositions at 20°C [wt. %]

Hydrocarbon-rich phase			Ammonia-rich phase		
Benzene	Sodium	Ammonia	Benzene	Sodium	Ammonia
87.3	0.02	12.7	2.1	14.1	83.9
77.1	0.05	22.9	2.6	12.5	84.9
69.0	0.1	30.9	3.5	11.0	85.5
51.7	0.3	48.0	4.2	9.3	86.5
47.5	0.4	52.1	5.3	8.6	86.1
37.3	0.7	62.0	7.6	7.3	85.7
Plait point			13.6	4.2	82.2

Table 2 Cyclohexen-sodium-ammonia equilibrium compositions at 20°C [wt. %]

Hydrocarbon-rich phase			Ammonia-rich phase		
Cyclohexene	Sodium	Ammonia	Cyclohexene	Sodium	Ammonia
90.61	0	9.39	17.81	0	82.19
91.0	0.02	9.0	12.7	2.1	85.2
91.8	0.02	8.2	8.3	2.9	88.8
91.9	0.03	8.1	5.3	5.6	89.1
92.4	0.04	7.8	3.9	8.9	87.2
95.4	0.02	4.6	1.6	13.7	84.7

in Fig. 1. After filtration of the almost insoluble sodium hydroxide, a part of this solution was transferred through the valve joint into a measuring bottle of about 50 cc volume, already containing about 10 grams of hydrocarbon. Care was taken to evacuate and desiccate the measuring bottle and the connecting parts to avoid contamination of the system with air and water vapor.

Ternary liquid-liquid equilibria were determined by a method slightly modified from those reported in the previous paper⁵. First, the composition of sodium-liquid ammonia solution was determined by chemical analysis, and secondary hydrocarbon was introduced and weighed. Liquid compositions were corrected slightly for the amount of components existing as vapor by measuring the volume of vapor space and total pressure, assuming that the concentrations of hydrocarbons could be neglected in the vapor phase.

An aliquot of homogeneous ammonia-rich phase in a measuring bottle, in equilibrium at 20°C, was effused carefully and slowly into another evacuated pressure bottle (receiver) through a syringe needle. A trace of solution in the connecting part was washed into the receiver by liquid ammonia condensed at that part which distilled off from the receiver until the blue color disappeared. Then, ammonia was evaporated through the needle valve and absorbed in 2N sulfuric acid solution. The concentration of ammonia was found by titrating the excess sulfuric acid of 2N acid solution which absorbed all ammonia with 0.5N sodium hydroxide solution using methylred as an indicator. Sodium metal in receiver was converted to sodium methylate and titrated with 0.1N hydrochloric acid. Thus the composition of ammonia-rich phase was found. The composition of hydrocarbon-rich phase was determined in a similar way.

Fig. 1 Glass bottle having a glass filter

Fig. 2 Benzene-sodium-ammonia system at 20°C, wt. fraction

Fig. 3 Cyclohexen-sodium-ammonia system at 20°C, wt. fraction

Results and Discussion

The experimental results for the systems benzene-sodium-ammonia and cyclohexene-sodium-ammonia at 20°C are given in Tables 1 and 2, and are plotted in Figs. 2 and 3, respectively. The obtained tie lines pass through the points representing total mixtures, and material balance checks satisfactorily. Tie-line data for the former system in the range of liquid phase are fairly well correlated by Hand²,

Fig. 4 Schematic diagram for transformation of the coordinates

Fig. 5 Variation of relationships between x_3''/x_1'' and $\bar{x}_3/\bar{x}_1$ depending on the values of w/kT

Othmer⁷⁾ and Ishida³⁾ coordinates. Plait point was estimated according to Treybal et al.⁸⁾.

As will be clear from Figs. 2 and 3, it is observed that the increasing concentration of sodium in the mixtures decreases the solubilities of hydrocarbon in liquid ammonia, and solid phase appears. This is illustrated in Fig. 4. The solid phase will appear in the range of triangle ADO. In this paper we will discuss the range of liquid-liquid phase.

Since $\overline{OA}$ and $\overline{OC}$ are considered to be base lines in skew coordinates in Fig. 4, $\overline{AD}$ is represented by

$$X_3 = px'_1 + q \quad (1)$$

where x'_1 denotes the weight fraction of hydrocarbon and p and q are defined from solubility of sodium in liquid ammonia at a given temperature. For this system at 20°C, p and q are -0.819, and 0.819, respectively⁹⁾. The concentration of the third component (ammonia) more than $\overline{AD}$ may be represented by

$$x_3^o = x'_3 - X_3 \quad (2)$$

Table 3 Estimated values in the three condensed phase region [wt. %]

Benzene-sodium-ammonia system

	Benzene	Sodium	Ammonia
E*	1.0	17.9	81.1
F*	99.99	0.002	0.009

* These points are shown in Fig. 4.

Then, the new weight fraction is defined as follows

$$x_1 = \frac{x'_1}{x'_1 + x'_2 + x'_3}, \quad x_2 = \frac{x'_2}{x'_1 + x'_2 + x'_3}, \quad x_3 = \frac{x'_3}{x'_1 + x'_2 + x'_3} \quad (3)$$

Applying the above correlation, it is possible to transform the coordinates of the phase diagram into liquid phase region only. The treatment of these systems will be entirely the same as those of the previous paper⁴⁾, where the method of correlating ternary liquid equilibrium data with the theory of regular solution has already been discussed. In the zeroth approximation, which is the simplest solution of the theory, the conjugated phase in cases of the symmetrical type with respect to component 1 and 2 are obtained from Eq.(4)

$$\frac{\bar{x}_3}{\bar{x}_1} = \frac{(\bar{x}_2/\bar{x}_1 - 1)w/kT}{\ln(\bar{x}_2/\bar{x}_1)} - \left(\frac{\bar{x}_2}{\bar{x}_1} + 1\right) \quad (4)$$

in which $\bar{x}$ is weight fraction of components and w is interchange energy of a pair of nearest neighbors, one being of species 1 and the other species 2, k is the Boltzmann constant and T is absolute temperature. The value of w/kT may be obtained from the mutual solubility data of the nonconsolute component with

$$\frac{w}{kT} = \left[\frac{\ln \bar{x}_2 - \ln \bar{x}_1}{\bar{x}_2 - \bar{x}_1} \right]_0 \quad (5)$$

where the subscript ₀ refers to the binary solutions of the diluent 2, and the solvent 1. However, the accurate evaluation of the parameter might be difficult from mutual solubility data in cases of sparingly soluble mixtures, or from data determined by impure reagents for the solvent or the diluent contaminated with the solute.

Rewriting Eq.(5)

$$\frac{w}{kT} = \frac{1}{\frac{\bar{x}_2 - \bar{x}_1}{\ln \bar{x}_2 - \ln \bar{x}_1}} = \frac{1}{\bar{x}_{lm}} \quad (6)$$

the parameter w/kT may be estimated as the reciprocal of logarithmic mean of $\bar{x}_1$, and $\bar{x}_2$. In other words, since parameter w/kT is assumed constant at a constant temperature in the theory, the solubility of diluent and solvent in symmetrical regular ternary mixtures can be estimated from the logarithmic mean of $\bar{x}_1$ and $\bar{x}_2$ with $\bar{x}_1 + \bar{x}_2 = 1$. Accordingly, the value of w/kT might be evaluated from the linear plots of x_3''/x_1'' against $\bar{x}_3/\bar{x}_1$ on log-log coordinates: smaller values of the parameter will give concave curves and greater values convex curves, as shown in Fig. 5. For the system benzene-sodium-ammonia at 20°C, the value of w/kT was estimated to 6.8.

Another parameter b at the zero concentration of

the solute in Eq.(4) in the previous paper may be evaluated graphically or from values of more than three ternary data by the equation derived from Eq.(14) in the previous paper⁴⁾.

$b_0 =$

$$\frac{b_j(b_i - b_k)(M_i - M_j)(M_k - M_0) - b_k(b_i - b_j)(M_i - M_k)(M_j - M_0)}{(b_i - b_k)(M_i - M_j)(M_k - M_0) - (b_i - b_j)(M_i - M_k)(M_j - M_0)} \quad (7)$$

where $M = \bar{x}_2/\bar{x}_1$, and subscripts i, j, k represent the respective ternary data, and suffix $_0$ denotes the binary value of zero concentration of the solute. For the system benzene-sodium-ammonia at 20°C, the value of b was estimated as 48. Estimated values in the three condensed phase region are given in **Table 3**. It seems that these values would be probable, and the method described above will be useful for the estimation of solubilities in the case of sparingly soluble mixtures.

Acknowledgement

The authors would like to thank the Chiyoda Chemical Engineering & Construction Co., Ltd., for financial support of these experimental investigations.

Nomenclature

b = constant
 d_4^{20} = specific gravity at 20°C
 k = Boltzmann constant

M = $\bar{x}_2/\bar{x}_1$
 n_D^{20} = refractive index
 p, q = constant
 T = absolute temperature
 w = interchange energy of pair of nearest neighbors
 x = weight fraction of component after transformed coordinates
 x, x' = weight fraction of component
 $\bar{x}$ = weight fraction of component for symmetrical ternary regular mixtures
 x° = the quantity defined by Eq.(2)
 X = the quantity defined by Eq.(1)
 <Subscripts>
 0 = values for binary mixtures of component 1 and 2
 1, 2, 3 = kind of component
 i, j, k = kind of data

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DISSOCIATION PRESSURE OF SO₂-QUINOLCLATHRATE AND A METHOD FOR ITS DETERMINATION*

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A method of general applicability and reasonable accuracy for the determination of the dissociation pressure of quinolclathrate is proposed.

The attainment of equilibrium is remarkably accelerated by gas circulation and by the addition of liquid to the gas-solid system.

The dissociation pressures of sulfur dioxide-quinolclathrate were determined in a temperature range of 0°C to 60°C, and ΔH_{298}° , ΔG_{298}° and ΔS_{298}° were calculated.

Introduction

Petroleum refining capacity in Japan approached the 3,500,000 barrels-per-day level in 1970, while that in 1965 was 1,440,000 barrels. At the same

time, air pollution caused by sulfur dioxide has already become a social problem. To solve this, many attempts have been made, and the authors' object is the removal and recovery of hydrogen sulfide and sulfur dioxide which are the byproducts of petroleum refineries and other chemical industries.

It was found by preliminary experiment that hydrogen sulfide and sulfur dioxide were crystallized as quinolclathrate from aqueous solution of hydroquinone (often called quinol). These crystals may be de-

* Received on February 20, 1970

Presented at the 32nd Annual Meeting of the Society of Chemical Engineers, Japan, April 1967