- Design and Develop.*, **12**, 271 (1973).
- 20) Mertl, I.: *Coll. Czech. Chem. Comm.*, **37**, 366 (1972).
 - 21) Morisue, T., K. Noda and K. Ishida: *J. Chem. Eng. Japan*, **5**, 219 (1972).
 - 22) Nelder, J. and R. Mead: *Computer J.*, **7**, 308 (1965).
 - 23) Nitta, T. and T. Katayama: *J. Chem. Eng. Japan*, **8**, 89 (1975).
 - 24) Ostrowski, A. M.: "Solution of Equations and Systems of Equations", Academic Press, New York (1966).
 - 25) Palmer, D. A. and B. D. Smith: *J. Chem. Eng. Data*, **17**, 71 (1972).
 - 26) Prausnitz, J. M.: "Molecular Thermodynamics of Fluid-Phase Equilibria", Prentice Hall, Inc., Englewood Cliffs, N. J. (1969).
 - 27) Prausnitz, J. M., C. A. Eckert, R. V. Orye and J. P. O'Connell: "Computer Calculations of Multicomponent Vapor-Liquid Equilibria", Prentice Hall, Inc., Englewood Cliffs, N. J. (1967).
 - 28) Renon, H. and J. M. Prausnitz: *AIChE J.*, **14**, 135 (1968)
 - 29) *ibid.*, **15**, 785 (1969).
 - 30) Renon, H. and J. M. Prausnitz: *Ind. Eng. Chem., Process Design and Develop.*, **7**, 220 (1968).
 - 31) Scatchard, G.: *Chem. Revs.*, **8**, 321 (1931).
 - 32) Scatchard, G. and C. L. Raymond: *J. Am. Chem. Soc.*, **60**, 1278 (1938).
 - 33) Scatchard, G. and L. B. Ticknor: *ibid.*, **74**, 3724 (1952).
 - 34) Schmidt, G. C.: *Z. physik. Chem.*, **99**, 71 (1921).
 - 35) Smith, V. C. and R. L. Robinson: *J. Chem. Eng. Data*, **15**, 391 (1970).
 - 36) Stephen, H. and T. Stephen: "Solubility of Inorganic and Organic Compounds", Vol. 1, Macmillan Co., New York (1963).
 - 37) Yasuda, M., H. Kawade, and T. Katayama: *Kagaku Kogaku Ronbunshu*, **1**, 172 (1975).
 - 38) Wilson, G. M.: *J. Am. Chem. Soc.*, **86**, 127 (1964).

VAPOR-LIQUID EQUILIBRIUM RELATIONS FOR THE SYSTEM ACCOMPANIED BY HYPOTHETICAL CHEMICAL REACTION CONTAINING SALT

YASUhide NISHI

Faculty of Engineering, Ehime University, Matsuyama, 790

In a system accompanied by hypothetical chemical reaction vapor-liquid equilibrium ratio, K_i , of component i has been expressed by

$$\log K_i = -A_i/T + B_i$$

where T is the absolute temperature, A_i is a constant determined by reaction system and component i , and B_i is a constant determined from vapor-liquid equilibrium data for the liquid composition at conversion 0 and/or 1. The object of this paper is to show that the equation mentioned above can also be applied to the system including salt. Following two systems are herein discussed:

i-propanol-*n*-propanol-calcium chloride
methanol-ethanol-water-calcium chloride

In these systems A_i implies the salt effect, but its behavior was not definitely observed.

Introduction

Salts may be used as a separating agent for distillation or a catalyst in the operation of distillation accompanied by chemical reaction. It may be therefore useful to investigate the salt effects for vapor-liquid equilibria of systems accompanied by chemical reaction.

The author^{3,4)} has previously reported that vapor-liquid equilibrium relations for systems accompanied by hypothetical chemical reaction could be expressed in the same way as for a system accompanied by

chemical reaction. That is, in a system accompanied by chemical or hypothetical chemical reaction vapor-liquid equilibrium ratio, K_i , for component i is correlated by

$$\log K_i = -A_i/T + B_i \quad (1)$$

where T is the absolute temperature, A_i is a constant determined by reaction system and component i , and B_i is a constant determined from vapor-liquid equilibrium data for the liquid composition at conversion 0 and/or 1. If vapor-liquid equilibrium relations for their liquid compositions are known, vapor-liquid equilibrium relations for the system accompanied by chemical reaction can be predicted. The object of the present paper is to show that the equation can be applied to systems including salt.

Received August 12, 1974.

* Presented at the 7th Autumn Meeting (at Nagoya, October 1973) and at the Hokuriku Meeting (at Toyama, July 1974) of the Soc. of Chem. Engrs., Japan.

Calcium chloride is used as a dissolved salt and the following two systems are herein discussed:

System A:

i-propanol-*n*-propanol-calcium chloride

System B:

methanol-ethanol-water-calcium chloride

System A

For the system without salt in System A, vapor-liquid equilibrium data have been obtained by Ballard *et al.*¹⁾ The author⁴⁾ has correlated their results by Eq. (1). In this study, the applicability of Eq. (1) to the system including salt and the salt effects for the parameter A_i were investigated. The concentrations of the salt were 2.0, 4.0, 7.0, 10.0, 13.0 and 16.7 wt% on a salt-free basis.

System B

For the system without salt in System B, vapor-liquid equilibrium relations could be predicted from vapor-liquid equilibrium data for the binary systems at conversion 0 and 1 by the author³⁾, where the hypothetical chemical reaction was as follows:

For the System B the same study as in the case of System A was also made under the salt concentration 16.7 wt%, where the x - y - t data for the system MeOH-EtOH-CaCl₂ and the System B refer to those by Ohe *et al.*^{5,6)}. For the systems MeOH-H₂O-CaCl₂ and EtOH-H₂O-CaCl₂, observations under the salt concentration have not been made. However, for the former system the ratio of relative volatility including the salt has been correlated with the equation by Yoshida *et al.*⁹⁾

$$\log \alpha_s / \alpha = 4.77N \quad (3)$$

whereas for the latter system it has been used by Hashitani *et al.*²⁾

$$\log \alpha_s / \alpha = 1.3N + 0.34 \quad (4)$$

Using these equations, the x - y relations under the salt concentration are predictable, but the x - t relations are not predictable. In the present investigation the x - y - t measurements were therefore performed for these two systems under the salt concentration 16.7 wt%.

Experimental

The experimental apparatus and method used in the present investigation were essentially the same as those described by Ohe *et al.*^{5,6)}. Vapor compositions for the systems MeOH-H₂O-CaCl₂ and EtOH-H₂O-CaCl₂ were determined by measurement of their densities. For System A, these were determined from gas chromatography. As a dissolved salt, anhydrous calcium chloride was used. However, if available, dihydrous salt of calcium chloride was also used. These reagents were special grade and were used without further purification.

Results and Discussion

System A

Table 1 shows experimental x - y - t data. Figs. 1 and 2 show x - y and x - t diagrams. Fig. 3 is a plot of $\log K_i$ against $1/T$. Linear relations are obtained as shown in Fig. 3, from which it can be seen that Eq. (1) is applicable to the system including salt. Constants A_i and B_i were determined by using a least squares method, and are shown in Table 2.

Using these obtained A_i and B_i values, the values of y_i and t corresponding to experimental liquid compositions were predicted and the calculated results were compared with the observed values with Eq. (5).

$$\begin{aligned} \varepsilon_y &= |y_{\text{obs}} - y_{\text{calc}}|_{\text{av}} \\ \varepsilon_t &= |t_{\text{obs}} - t_{\text{calc}}|_{\text{av}} \end{aligned} \quad (5)$$

The values of ε_y and ε_t are also shown in Table 2. These values for the system *i*PrOH-*n*PrOH have been reported by the author⁴⁾, and are also shown in Table 2. Since the maximum values of ε_y and ε_t are 0.71 mol% and 0.47°C, it was found that Eq. (1) is applicable to the system including salt.

Varying the salt concentration, the values of constant A_i have slight variation from the values for the system without salt, but have no definite trend of increase or decrease with salt concentration. It may be therefore concluded that the parameter A_i is not affected by salt addition in System A. This is the value determined from the heat of vaporization of each component⁴⁾. In System A, the variation of boiling point due to salt addition is slight. Hence, it may be that the salt effect for the heat of vaporization is slight.

MeOH-H₂O-CaCl₂ and EtOH-H₂O-CaCl₂ systems

Table 3 shows the experimental results for MeOH-H₂O-CaCl₂ and EtOH-H₂O-CaCl₂ systems. Fig. 4 shows x - y diagram for the former system and Fig. 5, for the latter system. Fig. 6 shows x - t diagrams for these systems. The curves for the salt concentrations not shown in these figures are nearly in the middle of these curves. As can be seen from Figs. 4 to 6 there is no difference between anhydrous and dihydrous calcium chloride.

The vapor compositions predicted from Eq. (3) are shown with a full line in Fig. 4. The predicted results agree well with the experimental results, and the average deviation between observed and calculated compositions was 0.72 mol%. Eq. (3) is therefore applicable to the system at the salt concentration 16.7 wt%.

As shown in Fig. 5 with a dash-dot line, the vapor compositions predicted from Eq. (4) do not agree with the experimental results. So the author plotted $\log \alpha_s / \alpha$ against N , which is shown in Fig. 7. As can be seen from Fig. 7, the relation can be expressed by

Table 1 Vapor-liquid equilibrium data for *i*-propanol-*n*-propanol with CaCl₂ at 1 atm

CaCl ₂ [wt %]	2.0	4.0	7.0	10.0	13.0	16.7
x_1	y_1	t [°C]	y_1	t [°C]	y_1	t [°C]
0.0	0.000	100.5	0.000	98.7	0.000	100.0
0.1	0.159	98.0	0.159	96.5	0.149	97.0
0.2			0.300	94.3		
0.3	0.387	94.8	0.412	94.0	0.428	93.8
0.4			0.528	92.0		
0.5	0.620	91.0	0.634	90.0	0.642	91.2
0.6			0.717	89.0		
0.7	0.798	87.1	0.806	88.0	0.806	87.2
0.8			0.880	87.0		
0.9	0.937	85.8	0.948	84.0	0.946	85.0
1.0	1.000	(82.8)	1.000	(83.4)	1.000	(83.6)

() ; These values are obtained from a smoothed curve using data in the literature^{5,6}.

Table 2 Calculated A_i , B_i , ε_y and ε_t values

CaCl ₂ [wt %]	0.0*	2.0	4.0	7.0	10.0	13.0	16.7
A_1 [°K]	2520	1613	1955	1766	2019	2386	2078
B_1	7.077	4.523	5.481	4.955	5.649	6.667	5.807
A_2 [°K]	2322	1808	2550	2329	2500	2592	2768
B_2	6.271	4.846	6.874	6.255	6.705	6.941	7.402
ε_y [mol %]	0.57	0.71	0.48	0.40	0.25	0.39	0.52
ε_t [°C]	0.21	0.46	0.43	0.47	0.29	0.26	0.33

* from previous paper⁴)

Table 3 Vapor-liquid equilibrium data for methanol (1)-water (2) and ethanol (1)-water (2) systems with CaCl₂ 16.7 wt % at 1 atm

Systems	Methanol-water		Ethanol-water	
x_1	y_1	t [°C]	y_1	t [°C]
0.000	0.000	102.80	0.000	102.80
0.020			0.271	96.00
0.040			0.389	91.60
0.050	0.364	93.60		
0.100	0.487	88.10	0.542	85.00
0.150	0.563	84.45		
0.200	0.651	81.00	0.647	82.45
0.300	0.736	77.80	0.694	81.45
0.400	0.791	76.00	0.753	81.25
0.500	0.839	73.65	0.795	80.70
0.600	0.875	72.80	0.828	81.50
0.700	0.913	71.00	0.867	81.50
0.800	0.936	70.20	0.915	82.40
0.900	0.969	69.40	0.942	81.65

a linear line in this experimental region, and Eq. (6) was obtained by a least squares method.

$$\log \alpha_s / \alpha = 6.00N + 0.013 \quad (6)$$

Eq. (4) was obtained for saturation or near saturation of salt, that is, $N > 0.16$, and the range of salt concentration differs from that of the present investigation. Since N lies from 0.026 to 0.062 in the salt concentration 16.7 wt % and α_s / α is 1 where N is zero, it appears likely that Eq. (6) is applicable to this experimental condition. The average deviation between observed and calculated values of vapor composition is 0.42 mol %.

Prediction of vapor-liquid equilibria for system B

Vapor-liquid equilibria for System B are predictable by the same method as for the system accompanied by hypothetical chemical reaction without salt. Then the vapor-liquid equilibrium data used of the ternary

Fig. 1 x - y diagram for the system *i*PrOH-*n*PrOH-CaCl₂

Fig. 2 x - t diagram for the system *i*PrOH-*n*PrOH-CaCl₂

Fig. 3 $\log K_i$ vs. $1/T$ for the system *i*PrOH-*n*PrOH-CaCl₂

Fig. 4 x - y diagram for the system MeOH-H₂O-CaCl₂

Fig. 5 x - y diagram for the system EtOH-H₂O-CaCl₂

systems at conversion 0 and/or 1 are as follows:

1. MeOH-EtOH-CaCl₂ system (salt concentration 16.7 wt %); x - y - t data by Ohe *et al.*⁵⁾
2. MeOH-H₂O-CaCl₂ system (salt concentration 16.7 wt %); x - y relation calculated by Eq. (3), and x - t data observed by the author
3. EtOH-H₂O-CaCl₂ system (salt concentration 16.7 wt %); x - y relation calculated by Eq. (6) and x - t data observed by the author.

Vapor-liquid equilibrium data for the system without salt, which is necessary in Eqs. (3) and (6), are those by Uchida *et al.*⁸⁾ for MeOH-H₂O system and by Rieder *et al.*⁷⁾ for EtOH-H₂O system.

The predicted results were compared with the observed results by Ohe *et al.*⁶⁾. The calculated results agree well with the observed results except for only one run*, and the average deviations were 1.25 mol % for y_1 , 1.32 mol % for y_2 , 1.05 mol % for y_3 and 0.48°C for temperature. In these calculations best predicted results were obtained by the use of the values 1,700 for A_1 , 2,900 for A_2 and 1,900 for A_3 . Since these values are equal or nearly equal to A_i values for the

* This is a datum of line 16 in Table 1 in Ref.⁶⁾ ($x_1=0.543$, $x_2=0.377$, $y_1=0.355$, $y_2=0.626$, $t=77.7^\circ\text{C}$) and may be a misprint.

Fig. 6 x - t diagram for the systems MeOH-H₂O-CaCl₂ and EtOH-H₂O-CaCl₂

Fig. 7 $\log \alpha_s/\alpha$ vs. N for the system EtOH-H₂O-CaCl₂

system without salt⁸⁾ ($A_1=1,700$, $A_2=2,300$ and $A_3=1,700$), it may be concluded that the parameter A_i is not affected by salt addition in System B.

Conclusions

In the system *i*PrOH-*n*PrOH-CaCl₂, vapor-liquid equilibria are correlated by Eq.(1), which has been obtained for the system *i*PrOH-*n*PrOH. The values of constant A_i are slightly affected by the salt concentration. Vapor-liquid equilibria at a salt concentration can, therefore, be predicted from boiling-point data of each alcohol at the given value of salt concentration.

At the concentration of calcium chloride 16.7 wt %, vapor-liquid equilibria are expressed for the system MeOH-H₂O-salt by Eq. (3) and for the system EtOH-H₂O-salt by Eq. (6).

Vapor-liquid equilibria for the system MeOH-EtOH-H₂O-CaCl₂ at a salt concentration can be predicted from x - y - t data for three ternary systems (including salt at the given value of salt concentration) using Eq. (1) as the same way as for the system without salt.

Nomenclature

A	= constant in Eq. (1)	[°K]
B	= constant in Eq. (1)	[—]
K	= vapor-liquid equilibrium ratio	[—]
N	= mole fraction of salt in liquid phase	[—]
T	= absolute temperature	[°K]

x	= mole fraction in liquid phase (salt-free basis)	[—]
y	= mole fraction in vapor phase	[—]
α	= relative volatility of binary mixture	[—]
α_s	= relative volatility of binary mixture containing salt	[—]
<Abbreviations>		
MeOH	= methanol	
EtOH	= ethanol	
PrOH	= propanol	
<Subscripts>		
1 and 2	= <i>i</i> PrOH and <i>n</i> PrOH for System A	
1, 2 and 3	= MeOH, EtOH and H ₂ O, respectively for System B	
i	= component i	

Literature Cited

- 1) Ballard, L. H. and M. V. Winkle: *Ind. Eng. Chem.*, **42**, 2450 (1952).
- 2) Hashitani, M., M. Hirata and Y. Hirose: *Kagaku Kōgaku*, **32**, 182 (1968).
- 3) Nishi, Y.: *J. Chem. Eng. Japan*, **6**, 220 (1973).
- 4) Nishi, Y.: *Nippon Kagaku Kaishi*, **1973**, 1592 (1973).
- 5) Ohe, S., K. Yokoyama and S. Nakamura: *Kagaku Kōgaku*, **35**, 104 (1971).
- 6) Ohe, S., K. Yokoyama and S. Nakamura: *ibid.*, **34**, 325 (1970).
- 7) Rieder, R. M. and A. R. Thompson: *Ind. Eng. Chem.*, **41**, 2905 (1949).
- 8) Uchida, S. and H. Kato: *Kogyo Kagaku Zasshi (J. Chem. Soc., Japan, Ind. Chem. Sec.)*, **37**, 525 (1934).
- 9) Yoshida, F., A. Yasunishi and Y. Hamada: *Kagaku Kōgaku*, **28**, 133 (1964).

ISOTHERMAL VAPOR-LIQUID EQUILIBRIUM DATA OF ISOPROPANOL-WATER SYSTEM

EIZO SADA AND TETSUO MORISUE

Department of Chemical Engineering, Nagoya University,
Nagoya, 464

Total pressure for the system of isopropanol and water was measured in a temperature range from 35 to 75°C by using a modified Othmer recirculation still. The vapor-liquid equilibrium was calculated from the total pressure-composition data by using the numerical method of Barker. Simultaneous fitting of the excess Gibbs energy and the excess enthalpy data was successfully done by using the Wilson equation.

Introduction

This research forms a part of our investigation concerned with salt effect on vapor-liquid equilibrium.

The system of isopropanol and water is theoretically and practically important, and not a little information in this system is already available. Belousov and Ponner³⁾ found that the dependence of excess enthalpy (heat of mixing) on concentration has an S-shaped character, and the excess enthalpy increases remarkably with increasing temperature. This result was also confirmed by other investigators³⁾. The values of excess volume are negative over the whole concentration region⁵⁾. Wilson and Simons¹¹⁾, who measured the isobaric vapor-liquid equilibria at low pressures, found that isopropanol forms a homogeneous azeotrope with water. This binary system is strongly non-ideal and the deviation from the

ideal solution is positive. Barr-David and Dodge²⁾ measured the isothermal vapor-liquid equilibria at 150 to 300°C.

In this paper, the total vapor pressure of the isopropanol-water solution is measured by a dynamic method using the modified Othmer still. From the experimental results the vapor-liquid equilibrium is evaluated at each temperature by using the numerical method, and furthermore the excess Gibbs energy and the excess enthalpy are simultaneously fitted by using the Wilson equation¹²⁾. Also, the vapor-liquid equilibrium is measured under atmospheric pressure to check the consistency of the experimental apparatus.

Experimental

Apparatus and procedure

A modified equilibrium still of the Othmer type⁷⁾ was used for the measurement of vapor-liquid equilibrium. The total volume of the still is about 400 cm³

Received August 15, 1974.