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Influence of Nonvolatile Solute on Boiling Point of Azeotrope*

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Abstract The influence of 10 nonvolatile solutes on boiling point of methanol-tetrahydrofuran azeotrope was determined by means of isobaric vapor-liquid equilibrium experiments. Based on classical thermodynamics a conclusion of universal significance was derived, i. e., a little nonvolatile solute always causes the elevation of azeotrope's boiling point irrespective of the variation of its vapor composition. It is in agreement with the experimental results and the relevant reports in the literature without exception.

Key words Methanol, Tetrahydrofuran, Nonvolatile solute, Azeotrope, Boiling point

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1 Introduction

The influence of nonvolatile solute on boiling point of liquid mixtures is of important significance in guiding scientific researches and production practices. As everybody knows, nonvolatile solute always causes the boiling point elevation in pure solvent, however, anomalous variation of boiling point depression is possible as well sometimes in mixed solvent^[1,2]. Nevertheless, a literature survey shows that nonvolatile solute always causes the boiling point elevation of azeotrope, such as the boiling point elevation caused by various salts in ethanol-water azeotrope^[3] and various nonvolatile solutes in methanol-acetone-chloroform azeotrope^[4]. Is it of universal significance? This conclusion was proved to be true in this paper because it not only can be derived from thermodynamics, but also consists with all known experimental results.

2 Experimental

2.1 Materials

All of the reagents used in this paper were analytical reagent grade. The solid nonvolatile solutes were dried at 120°C for 24 h prior to experiments. Methanol and tetrahydrofuran were further purified according to the standard method, their refraction indexes (n_D^{20}) were 1.3286 and 1.4070, respectively.

2.2 Apparatus and procedure

All vapor-liquid equilibrium measurements were made by using a modified recirculation still of Othmer type for salt effect studies. Details of the still and experimental procedure are described^[2]. The internal pressure of the still was maintained at constant value (100.3 kPa) by linking a set of pressure stabilizing apparatus and monitored by using a digital display barometer. The boiling point of mixed solvent was measured by using a mercury-in-glass thermometer (1/10°C divisions) and the elevation of azeotrope's boiling point by using the Beckmann thermometer. The equilibrium vapor composition was determined by means of refrac-

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tion measurements, and an Abbe refractometer of WZS-1 type with accuracy of 0.0003 was used. The azeotropic composition of methanol-tetrahydrofuran binary liquid mixture was obtained by means of measuring $x \sim v$ curve. The binary solution's vapor-liquid equilibrium data were deemed thermodynamic consistent by the Herington method.

2.3 Results

The VLE data of methanol-tetrahydrofuran azeotrope and the comparison with the literature value are shown in Table 1. The data of influence of 10 nonvolatile solutes on the boiling point of methanol-tetrahydrofuran azeotrope are given in Table 2, in which the explanation of [Y] and [A] staying behind.

Table 1 Vapor-liquid equilibrium data of methanol₁-tetrahydrofuran₂ azeotrope

| $x_1(y_1)$ | $t/^\circ\text{C}$ | P/kPa | Taken from |
|------------|--------------------|----------------|------------|
| 0.476 | 60.45 | 100.3 | This paper |
| 0.476 | 60.82 | 101.3 | [1] |

3 Discussion

3.1 Thermodynamic consideration

When a kind of nonvolatile solute dissolves in an

Table 2 Influence of 10 nonvolatile solutes on boiling point of methanol₁-tetrahydrofuran₂ azeotrope ($x_1 = 0.476$, $P = 100.3$ kPa)

| Solute | $x_s \cdot 10^2$ | y_1 | $\Delta T/\text{K}$ | $-[Y][A]^{-1} \cdot 10^2$ | Solute | $x_s \cdot 10^2$ | y_1 | $\Delta T/\text{K}$ | $-[Y][A]^{-1} \cdot 10^2$ |
|---------------------------------|------------------|-------|---------------------|---------------------------|-------------------|------------------|-------|---------------------|---------------------------|
| Solute free | 0 | 0.476 | 0 | | Solute free | 0 | 0.476 | 0 | |
| LiCl | 1.03 | 0.458 | 0.148 | 12.12 | KOH | 1.04 | 0.442 | 0.104 | 39.70 |
| | 2.06 | 0.429 | 0.330 | 27.14 | | 2.08 | 0.419 | 0.250 | 49.16 |
| | 3.08 | 0.398 | 0.520 | 41.11 | | 3.12 | 0.379 | 0.410 | 57.78 |
| CuCl ₂ | 0.98 | 0.471 | 0.078 | 2.55 | NaI | 0.10 | 0.450 | 0.060 | 40.21 |
| | 1.96 | 0.465 | 0.180 | 4.31 | | 0.20 | 0.429 | 0.120 | 52.18 |
| | 2.94 | 0.459 | 0.324 | 5.38 | | 0.30 | 0.403 | 0.198 | 61.68 |
| KI | 0.44 | 0.472 | 0.038 | 3.59 | CaCl ₂ | 0.10 | 0.449 | 0.094 | 31.46 |
| | 0.88 | 0.466 | 0.088 | 7.30 | | 0.20 | 0.429 | 0.190 | 41.00 |
| | 1.32* | 0.461 | 0.124 | 10.47 | | 0.30 | 0.410 | 0.258 | 49.71 |
| NH ₄ NO ₃ | 0.68 | 0.472 | 0.044 | 2.79 | HgBr ₂ | 0.81 | 0.480 | 0.034 | 1.90 |
| | 1.37 | 0.467 | 0.076 | 6.37 | | 1.62 | 0.482 | 0.056 | 2.48 |
| | 2.05 | 0.462 | 0.132 | 7.84 | | 2.43 | 0.483 | 0.078 | 2.83 |
| NaBr | 0.36 | 0.469 | 0.036 | 9.11 | HgCl ₂ | 1.01 | 0.486 | 0.090 | 5.38 |
| | 0.72 | 0.461 | 0.070 | 16.38 | | 2.02 | 0.497 | 0.184 | 11.00 |
| | 1.08* | 0.457 | 0.088 | 19.89 | | 3.03 | 0.510 | 0.336 | 14.43 |

* Saturated.

azeotrope with constant composition at given pressure, the Gibbs-Duhem Eq. of liquid phase is as follows

$$\sum_{i=1}^K x_i d \frac{\mu_i}{RT} + x_s d \frac{\mu_s}{RT} = - \frac{H}{RT^2} dT \quad (1)$$

where subscripts i and s represent a component of azeotrope and nonvolatile solute, respectively; x_i is the mole fraction of component i in azeotrope, calculated on solute-free basis, so $\sum_{i=1}^K x_i = 1$ and $x_i (i = 1 \sim K)$ is constant; x_s is the mole ratio of solute to azeotrope; H is the enthalpy of solution containing 1 mol azeotrope. Suppose the chemical potentials of component i and solute s , viz., μ_i and μ_s , may be represented by fugacity f_i and activity a_s , respectively, it follows that

$$\mu_i = \mu_i^\circ(T) + RT \ln f_i \quad (i = 1 \sim K) \quad (2)$$

$$\mu_s = \mu_s^\circ(T, P) + RT \ln a_s \quad (3)$$

By substituting Eq. (2) and (3) into Eq. (1) and combining with

$$d \ln a_s = \left(\frac{\partial \ln a_s}{\partial x_s} \right)_{T, P} dx_s + \frac{H_s^\circ - \bar{H}_s}{RT^2} dT \quad (4)$$

where H_s° and \bar{H}_s are the molar enthalpy of solute at standard state and its partial molar enthalpy, respectively. It is found that

$$\sum_{i=1}^k x_i d \ln f_i + x_s \left(\frac{\partial \ln a_s}{\partial x_s} \right)_{T,P} dx_s = \left(\sum_{i=1}^k x_i \frac{\Delta_v \bar{H}_i}{RT^2} \right) dT \quad (5)$$

where $\Delta_v \bar{H}_i$ is the partial molar vaporization enthalpy of component i . Under condition of vapor-liquid equilibrium, $f_i = Py_i \varphi_i$, P , y_i , φ_i represent vapor's total pressure, the mole fraction of component i in vapor phase and its fugacity coefficient, respectively. Inserting above relationship into Eq. (5) and integrating Eq. (5) from $x_i = 0$ to x_s , recalling x_i ($i = 1 \sim K$) and P all are constant and φ_i may be taken as constant approximately, the result is as follows

$$[Y] + [A] = \int_T^{T'} \left(\sum_{i=1}^k x_i \frac{\Delta_v \bar{H}_i}{RT^2} \right) dT \quad (6)$$

where

$$[Y] = \sum_{i=1}^k x_i \ln \frac{y_i'}{y_i} \quad (7)$$

$$[A] = \int_0^{x_s} x_i \left(\frac{\partial \ln a_s}{\partial x_s} \right)_{T,P} dx_s \quad (8)$$

superscript s represents the system containing nonvolatile solute. Eq. (6) is the thermodynamic Eq. of nonvolatile solute's effect on the boiling point of azeotrope. Since the value in the parentheses on the right side of Eq. (6) is positive, if the sign of the left side is positive, the boiling point of containing nonvolatile solute system, viz., T' , must be higher than that of the system without any solute, viz., T , in other words, the boiling point must be elevated.

As for the sign of $[A]$, it depends on the sign of partial differential in Eq. (8). According to thermodynamics μ , or $\ln a_s$, must be an increasing function of x_s at constant temperature and pressure. If not so, solute should diffuse from the lower concentration region to the higher one when it dissolves in azeotrope, it is impossible. This means that not only the partial differential in Eq. (8), but also the value of $[A]$ are always positive, and $[A]$ will get more and more positive with increasing of integration limit x_s . Alternately, according to the theory of solution chemistry the logarithm of activity coefficient can be represented by a power series of liquid concentration^[5], i. e., $a_s = x_s \exp[f(x_s)]$. Inserting above relationship into Eq. (8) and recalling $f(x_s)$ is a power series of x_s , $[A]$ can be reduced to the power series of x_s , and the lowest order term of it

should be x_s . This implies $[A]$ is a small amount of the same order as x_s when x_s is not too large.

As to $[Y]$, let $\Delta y_i = y_i' - y_i$, thus $[Y]$ can be taken as a function of Δy_i through series expansion, viz.,

$$[Y] = \sum_{i=1}^k \frac{x_i}{y_i} \Delta y_i - \frac{1}{2} \sum_{i=1}^k \frac{x_i}{y_i^2} (\Delta y_i)^2 + \dots \quad (9)$$

For azeotrope $x_i = y_i$, and $\sum_{i=1}^k \Delta y_i = 0$, the first order term of Δy_i in Eq. (9) is equal to zero. The square term of Δy_i is always negative so that $[Y]$ is a small negative value. According to the phase rule the number of degrees of freedom is equal to 1 under this condition, so Δy_i may be regarded as a unitary function of x_s and must be proportional to it approximately when x_s is not too large. This means Δy_i is a small amount of the same order as x_s , and $(\Delta y_i)^2$ or $[Y]$ is a small amount of the higher order than x_s or $[A]$ when x_s is not too large. Therefore, the sign of the left side in Eq. (6) is mainly dominated by $[A]$, it must be positive, this implies that the boiling point of azeotrope must be elevated in dilute solution at least.

3.2 Discussion

The experimental results in Table 2 indicate that 10 nonvolatile solutes all cause the boiling point elevation of methanol-tetrahydrofuran azeotrope, although the variation of azeotrope's vapor composition caused by HgCl_2 and HgBr_2 is different from the others. The experimental results in this paper and the relevant reports in the literature^[3,4] are in agreement with above conclusion without exception.

Since the sign of $[Y]$ is opposite to $[A]$, the ratio of them was given in the fifth column of Table 2 in order to make comparison between their magnitudes. The calculation procedure is as follows: firstly, $[Y]$ was calculated out according to Eq. (7); then, the integration on the right side of Eq. (6) was calculated by assuming that $\Delta_v \bar{H}$ may be regarded as constant and replaced with the molar vaporization enthalpy; finally, $[A]$ was obtained by inserting the above results into Eq. (6). The molar vaporization enthalpy of methanol and tetrahydrofuran (taken from [6]) are 39215 and 27656 J/mol, respectively. It is evident that $[Y]$ is

always negative and its absolute value decreases at a faster pace than $[A]$ with approaching of x_1 to zero, therefore, $[A]$ becomes a primary factor dominating the variation of azeotrope's boiling point in dilute solution at least.

In fact, the boiling point of each azeotrope is still raised although the mean concentration of 10 nonvolatile solutes reaches 0.02, i. e., the mean value of x_1 is equal to 0.02, hence, the concentration of nonvolatile solute resulting in boiling point elevation is not limited to the narrow region without any practical significance. As concerns nonazeotropic mixtures, however, it is possible that $[Y]$ becomes negative and its absolute value is more than the value of $[A]$ even in dilute solution since the first order term in Eq. (9) may be not zero, in this case, the anomalous of boiling point depression will occur.

4 Conclusion

A conclusion of universal significance was derived

from thermodynamics, i. e., a little nonvolatile solute always causes the boiling point of azeotrope to increase. By verifying, it was in agreement with the experimental results in this paper and the relevant reports in the literature without exception.

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非挥发性溶质对共沸物沸点的影响*

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摘要: 测定了10种非挥发性溶质对甲醇-四氢呋喃共沸物沸点的影响. 发现与共沸物平衡的气相组成因非挥发性溶质不同发生了不同的变化, 但所有非挥发性溶质都引起共沸物沸点升高. 运用热力学原理对实验结果进行了讨论. 理论分析及对分析结果的实验检验表明, 少量非挥发性溶质总引起共沸物沸点升高是一个具有普遍意义的结论.

关键词: 甲醇; 四氢呋喃; 非挥发性溶质; 共沸物; 沸点

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