*Studies on Azeotropic Mixtures. III. Physical Basis of Azeotropic Correlation Rules**

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Introduction

Though several useful correlation rules of azeotropic data have been reported, they appear to lack in a common physical basis because the theory of azeotropes is little developed. It has been exemplified in part II¹⁾ that the molecular interchange energy w for azeotropes composed of one common component (azeotropic reagent) and the members of a homologous series was constant in a number of cases, applying Trouton's rule to such a series. Also, the equations

$$\varDelta_v S_1^0 (T_1^0 - T^a) = Nwx_2^2 \tag{1}$$

and

$$\varDelta_v S_2^0 (T_2^0 - T^a) = Nwx_1^2 \tag{2}$$

derived in part I²⁾ have proved to be useful in predicting azeotropic data. Here, T^a is the azeotropic point (for $p=1$ atm.), N, the Avogadro number, $\varDelta_v S_i^0$ the molar entropy of vaporization at boiling point T_i^0 (for $p=1$ atm.) of pure component ($i=1$ and 2), and x_1, x_2 mole fraction of both components respectively.

It will be shown in this paper that the equations (1) and (2) may give some information about the mutual relationship between independent correlation rules as well as their physical basis.

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* Partly presented at the 9th Annual Meeting of the Chemical Society of Japan held in Kyoto, April, 1956.

1) T. Yoshimoto and Y. Mashiko, This Bulletin, **30**, 56 (1957).

Relation between Boiling Points of Homologous Members and Azeotropic Composition

Now eliminating T^a between two equations (1) and (2), we have the following quadratic equation for x_2:

$$(S_2-S_1)x_2^2+2S_1x_2-\left\{S_1+\frac{S_1S_2}{W}(T_1^0-T_2^0)\right\}=0^{**} \tag{3}$$

This can be solved for x_2 to give

$$x_2=-\frac{S_1}{S_2-S_1}\pm\frac{\sqrt{S_1S_2}}{S_2-S_1}\left\{1+\frac{S_2-S_1}{W}(T_1^0-T_2^0)\right\}^{1/2}. \tag{4}$$

The necessary and sufficient condition for azeotrope existence is

$$-\frac{W}{S_2}<T_1^0-T_2^0<\frac{W}{S_1}, \tag{5}$$

as shown by us in part I and we see obviously $S_2-S_1<S_1$ in numerical values, so we can obtain readily

$$\left\{\frac{S_2-S_1}{W}(T_1^0-T_2^0)\right\}^2<1.$$

We may therefore develop (4) in convergent power series of $T_1^0-T_2^0$:

$$\begin{aligned}x_2=&\frac{\sqrt{S_1S_2}-S_1}{S_2-S_1}+\frac{\sqrt{S_1S_2}}{2W}(T_1^0-T_2^0)\\&+\frac{\sqrt{S_1S_2}(S_2-S_1)}{8W^2}(T_1^0-T_2^0)^2\\&+\frac{3\sqrt{S_1S_2}(S_2-S_1)^2}{48W^3}(T_1^0-T_2^0)^3+\cdots\cdots.\end{aligned} \tag{6}$$

Here, component 2 is chosen as a common azeotropic reagent, that is usually a more "associated" liquid, and must have larger entropy of vaporization than component 1. Lecat[3] obtained empirically a series of equations in the form

$$C=C_0+C_1\Delta+C_2\Delta^2$$

where C is wt. % of the second component, Δ the difference between boiling points of pure component, i.e. $T_1^0-T_2^0$, and C_0, C_1 and C_2 are all constants for a given series of homologous azeotropes. The equation (6) will thus interpret Lecat's empirical rule despite the fact that his rule differs in composition scale of azeotrope. If for example, the numerical values given in part II[1] for the series of azeotropes between 1-butanethiol and paraffinic hydrocarbons are introduced into equation (6), i.e., $S_1=20.3$, $S_2=22.0$ and $W=280$, we obtain

$$\begin{aligned}x_2=&0.49+0.038(T_1^0-T_2^0)\\&+0.000057(T_1^0-T_2^0)^2\\&+0.00000017(T_1^0-T_2^0)^3+\cdots\cdots.\end{aligned} \tag{8}$$

The coincidence of calculated curve with observed values is tested and the result shown in Fig. 1.

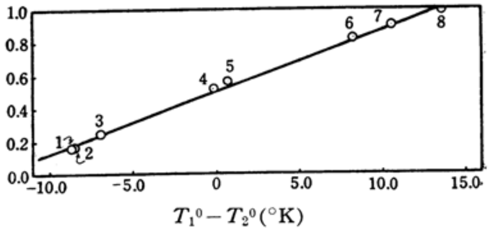

Fig. 1. Test of equation (8) for azeotropes of 1-butanethiol with paraffinic hydrocarbons: full line calculated, circles experimental. Paraffinic hydrocarbons: (1), 2, 3-Dimethylpentane; (2), 2-Methylhexane; (3) 3-Methylhexane; (4), *n*-Heptane; (5), 2, 2, 4-Trimethylpentane; (6), 2, 2-Dimethylhexane; (7), 2, 5-Dimethylhexane; (8), 3, 3-Dimethylhexane.

Azeotropic data are taken from R. L. Denyer, F. A. Fidler and R. A. Lowry, *Ind. Eng. Chem.*, **41**, 2727 (1949).

Since the boiling-point difference between components in this case is less than 14°C as judged by the discussion of azeotrope-forming range presented in part II[1], we may neglect the third and higher order terms and therefore obtain approximately

$$x_2=\frac{\sqrt{S_1S_2}-S_1}{S_2-S_1}+\frac{\sqrt{S_1S_2}}{2W}(T_1^0-T_2^0). \tag{9}$$

This will thus interpret the straight-line relationship between x_2 and T_1^0 proposed by Denyer et al[4]. The straight-line relationship is true in the azeotropes of organo-sulfur compounds such as thiol, sulfone, etc. with aliphatic hydrocarbons, where the difference between S_1 and S_2 is not so great.

In the limiting case where S_1 is equal to S_2, equation (6) reduces to

$$x_2=\frac{1}{2}\left\{1+\frac{S}{W}(T_1^0-T_2^0)\right\} \tag{10}$$

and then we have

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[2] T. Yoshimoto and Y. Mashiko, This Bulletin, **29**, 990 (1956).

** Hereafter the S_i and the W refer, for brevity, to $\Delta_v S^0{}_i$ and Nw respectively.

[3] L. H. Horsley, *Anal. Chem.*, **19**, 603 (1947).

[4] R. L. Denyer, F. A. Fidler and R. A. Lowry, *Ind. Eng. Chem.*, **41**, 2727 (1949); D. H. Desty and F. A. Fidler, ibid., **43**, 905 (1951).

$$x_1=\frac{1}{2}\left\{1-\frac{S}{W}(T_1^0-T_2^0)\right\}, \qquad (11)$$

where we write $S_1=S_2=S$ for brevity. The equations (10) and (11) are identical with those derived theoretically by Kuhn[5] for the azeotropes of dispersion force solutions where S_1 is approximately equal to S_2.

When T_1^0 is equal to T_2^0 in equation (9), we find

$$x_2=\frac{\sqrt{S_1S_2}-S_1}{S_2-S_1}<\frac{1}{2},$$

while x_2 is 1/2 in the limiting case where S_1 is equal to S_2.

Relation between Boiling Points of Homologous Members and Their Azeotropes with One Common Azeotropic Reagent

Another type of correlation is noticed in azeotropic data when we plot T^a against T_1^0. It has many advantages over the previous one especially in not needing any laborious analysis of azeotropic composition.

Eliminating x_1 and x_2 between two equations (1) and (2), we have a quadratic equation for $T_2^0-T^a$ in the form

$$\begin{aligned}\left(\frac{S_2}{W}-\frac{S_1}{W}\right)^2(T_2^0-T^a)^2&+2\left\{\frac{S_1^2}{W^2}(T_1^0-T_2^0)\right.\\ &\left.-\left(\frac{S_1}{W}+\frac{S_2}{W}\right)-\frac{S_1S_2}{W^2}(T_1^0-T_2^0)\right\}\\ &\times(T_2^0-T^a)+\left\{\frac{S_1^2}{W^2}(T_1^0-T_2^0)\right.\\ &\left.-2\frac{S_1}{W}(T_1^0-T_2^0)+1\right\}=0. \qquad (12)\end{aligned}$$

This can be solved for $T_2^0-T^a$ to give

$$T_2^0-T^a=\frac{-\left\{\frac{S_1^2}{W^2}(T_1^0-T_2^0)-\left(\frac{S_1}{W}+\frac{S_2}{W}\right)-\frac{S_1S_2}{W^2}(T_1^0-T_2^0)\right\}\pm\sqrt{4\frac{S_1S_2}{W^2}\left\{1+\left(\frac{S_2}{W}-\frac{S_1}{W}\right)(T_1^0-T_2^0)\right\}}}{\left(\frac{S_2}{W}-\frac{S_1}{W}\right)^2} \qquad (13)$$

Also noting that $\left\{\frac{S_2-S_1}{W}(T_1^0-T_2^0)\right\}^2<1$ and $S_2>S_1$, we may develop (13) in convergent power series of $T^0_1-T_2^0$:

$$\begin{aligned}T_2^0-T^a=&\frac{W}{(\sqrt{S_1}+\sqrt{S_2})^2}\\ &-\frac{\sqrt{S_1S_2}-S_1}{S_2-S_1}(T_1^0-T_2^0)\\ &+\frac{\sqrt{S_1S_2}}{4W}(T_1^0-T_2^0)^2\\ &-\frac{\sqrt{S_1S_2}(S_2-S_1)}{8W^2}(T_1^0-T_2^0)^3+\cdots\cdots. \qquad (14)\end{aligned}$$

When the numerical values for the series of 1-butanethiol-paraffinic hydrocarbon azeotropes are, as before, introduced into (14), we obtain

$$\begin{aligned}T_2^0-T^a=&3.31-0.49(T_1^0-T_2^0)\\ &+0.019(T_1^0-T_2^0)^2\\ &-0.000057(T_1^0-T_2^0)^3+\cdots\cdots. \qquad (15)\end{aligned}$$

The coincidence of calculated curve with observed values is tested and the result shown in Fig. 2.

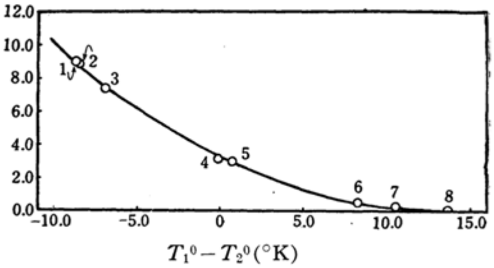

Fig. 2. Test of equation (15) for azeotropes of 1-butanethiol with paraffinic hydrocarbons: full line calculated, circles experimental.
Paraffinic hydrocarbons: see Fig. 1.

This will thus interpret Lecat's other empirical rule[6], i.e.,

$$\delta=A_0+A_1\Delta+A_2\Delta^2+A_3\Delta^3, \qquad (16)$$

where δ is the azeotropic depression $T_2^0-T^a$ and A_0, A_1, A_2 and A_3 are all constants for a given series of homologous azeotropes.†

† In the limiting case where S_1 is equal to S_2, we have from equation (14)

$$\begin{aligned}T_2^0-T^a=&\frac{W}{4S}-\frac{1}{2}(T_1^0-T_2^0)\\ &+\frac{S}{4W}(T_1^0-T_2^0)^2. \qquad (17)\end{aligned}$$

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[5] W. Kuhn and P. Massini, *Helv. Chim. Acta*, **33**, 737 (1950).

[6] M. Lecat, *Z. anorg. allgem. Chem.*, **186**, 123 (1930); L. H. Horsley, *Anal. Chem.*, **19**, 603 (1947). Similar explanation of this Lecat's rule was given by I. Prigogine and R. Defay, "Chemical Thermodynamics," Translated by D. H. Everett, Longmans (1954), p. 465.

This is identical with that derived by Kuhn[5] for dispersion force solutions if the third term is neglected, since it is not serious in such solutions.

The closer T_1^0 approaches T_2^0 in the equation (14), the more depression we have for azeotropic point and in the limit we have the maximum depression in the form

$$(T_2^0 - T^a)^{\max} = \frac{W}{(\sqrt{S_1}+\sqrt{S_2})^2}, \qquad (18)$$

where the depression implies the difference in boiling point of azeotrope and the lower boiling component. The maximum depression is therefore regarded as a measure of azeotrope-forming power of the series.

Skolnik[7] proposed a different type of correlation between T^a and T_1^0 in the form

$$\log (D - T^a) = E - F T_1^0, \qquad (19)$$

where D is the asymptotic value and E and F constants. For dispersion force solutions such as azeotropes formed by toluene with naphthene homologues, D is approximately T_2^0. The equation (19) is thus modified into

$$T_2^0 - T^a = A e^{-B(T_1^0 - T_2^0)}, \qquad (20)$$

where A and B are constants. If we assume

$$A = \frac{W}{4S}$$

and

$$B = \frac{2S}{W},$$

then we obtain

$$\begin{aligned} T_2^0 - T^a &= \frac{W}{4S}\, e^{-\frac{2S}{W}(T_1^0 - T_2^0)} \\ &= \frac{W}{4S}\left\{1 - \frac{2S}{W}(T_1^0 - T_2^0) + \frac{2S^2}{W^2}(T_1^0 - T_2^0)^2 - \cdots\cdots\right\} \\ &= \frac{W}{4S} - \frac{1}{2}(T_1^0 - T_2^0) + \frac{S}{2W}(T_1^0 - T_2^0)^2 - \cdots\cdots. \qquad (21) \end{aligned}$$

By comparing (21) with (17) we have an information on the physical meaning of Skolnik's constants E and F.

Summary

The physical meaning of four empirical correlation rules of azeotropic data, i.e. two types of Lecat's, Denyer et al.'s and Skolnik's rules, is clarified simultaneously with their mutual relations, by using the equations derived in part I and the assumption of constancy of molecular interchange energy for homologous azeotropes found in part II of the series of this study. The theoretically derived equations by Kuhn et al. are also given as a limiting case of ours.

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[7] H. Skolnik, *Ind. Eng. Chem.*, **40**, 442 (1948).