*Studies on Azeotropic Mixtures. I. General Considerations**

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Introduction

In 1900 Zawidzki[1] showed in his pioneering study on the liquid solutions that non-ideal binary solutions could be classified into two types with positive and negative deviations from Raoult's law. He also showed that when the two components of such solution had sufficiently equal vapor pressures, the positive type yielded a maximum point and the negative one a minimum point in the vapor pressure-composition curve. These points are called azeotropic points and the solutions are said, at such points, to form azeotropes or azeotropic mixtures. It is well known that the liquid phase of an azeotrope may be transformed to the vapor phase without changing the composition of any of these phases. This is a condition of practical importance, since it limits the possibility of separation by fractional distillation.

Recently Prigogine[2] has investigated azeotropic phenomenon assuming the solution to be regular. In this paper we will treat the same phenomenon along his line but from a more explicit standpoint of molecular interaction, with the aim of comparing the azeotrope-forming power of a number of solutions.

Our assumption is that an azeotropic mixture can be regarded as a strictly regular solution[3] near its boiling point, which can be treated with the quasi-crystalline model, introducing explicit representation for interaction energy of component molecules. Component molecules of the azeotropic mixture are usually more or less polar or non-spherically shaped and at a lower temperature they are prevented by their dipoles or shapes from executing free rotation. Thus it is by no means a good approximation to assume that they constitute a strictly regular solution, i.e., solution with spherical molecules of sufficiently equal size and of weak interaction energy. However, near its boiling point, the rotations of component molecules will become free enough to allow them to be regarded as constituting a strictly regular solution. Thus, near the boiling point, though all molecules distributed on each site of the quasi-crystalline lattice may not be always executing completely free rotation, their dipole or other figure axes are considered to orient at random.

The above assumption seems to be too crude to interpret the azeotropic phenomenon quantitatively, but some successes obtained in this paper suggest that we are not far from the right way. It may be mentioned that we have some suggestions[4] to interpret

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

[1] J. V. Zawidzki, *Z. physik. Chem.*, 35, 129 (1900).

[2] I. Prigogine and R. Defay, "Chemical Thermodynamics", Translated by D. H. Everett, Longmans (1954), chapt. XXVIII.

[3] E. A. Guggenheim, "Mixture", Oxford (1952), chapt. IV.

[4] R. S. Halford, *J. Chem. Phys.*, 8, 496 (1940); K. S. Pitzer, *J. Chem. Phys.*, 7, 583 (1939).

the deviation from Trouton's or Hildebrand's constant of real pure liquids by similar assumptions.

Derivation of Basic Formula for an Azeotropic Mixture

In the following study we will restrict our consideration to the binary solution. The molar Helmholtz free energy of pure components 1 and 2 is

$$\Delta_m F = RT(x_1 \ln x_1 + x_2 \ln x_2) + N x_1 x_2 w. \tag{1}$$

Here, x_i is the mole fraction of component $i (i=1, 2)$, T the absolute temperature, N the Avogadro number and R the gas constant. The equation is the zeroth approximation (treatment of random mixing) of the quasi-chemical treatment of strictly regular solution developed by Guggenheim[3] and it will be shown later that the approximation is quite reasonable within the range considered, so that we do not need further higher terms. w is a quantity determining the non-ideality of the solution and is called molecular interchange energy. We will give its explicit form in terms of the absolute average potential energy ε of the pair of molecules:

$$w = \frac{z}{2}(\varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12}). \tag{2}$$

z denotes the average number of nearest neighbors of a given molecule, i.e., the coordination number of the molecule on the quasi-lattice. In making a single exchange of molecule between liquid 1 and 2, we destory z 1–1 and z 2–2 pairs and form $2z$ 1–2 pairs of nearest neighbors, and the increase of potential energy is $2w$.

Denoting μ_i and γ_i the chemical potential and the activity coefficient of the ith component and the superscript o referring to the pure component, we obtain the chemical potentials from equation (1) by a usual procedure,

$$\mu_1 - \mu_1^0 = RT \ln x_1 + N x_2^2 w, \tag{3}$$

$$\mu_2 - \mu_2^0 = RT \ln x_2 + N x_1^2 w. \tag{4}$$

Further from the definition of the activity coefficient, we have

$$\mu_1 - \mu_1^0 = RT \ln x_1 \gamma_1, \tag{5}$$

$$\mu_2 - \mu_2^0 = RT \ln x_2 \gamma_2. \tag{6}$$

From these equations, we get

$$\ln \gamma_1 = \frac{Nw}{RT} x_2^2, \tag{7}$$

$$\ln \gamma_2 = \frac{Nw}{RT} x_1^2. \tag{8}$$

These are Hildebrand's relations for the regular solution and Nw corresponds to his constant B[5].

We will now turn to the equilibrium between the vapor and the liquid phase of binary azeotropic mixture[6]. In equilibrium state the chemical potentials of component i in both phases are equal:

$$\mu_i = \mu_{i'},$$

where

$$\mu_i = \mu_i^0 + RT \ln x_i \gamma_i, \tag{9}$$

$$\mu_{i'} = \mu_i^{0'} + RT \ln x_{i'} \gamma_{i'}. \tag{10}$$

In these equations a single prime refers to the vapor phase and no prime to the liquid one. Thus we obtain

$$\ln \frac{x_{i'} \gamma_{i'}}{x_i \gamma_i} = -\frac{\mu_i^{0'} - \mu_i^0}{RT}. \tag{11}$$

As the activity coefficient is the function of temperature and pressure, we obtain the following equation by considering an infinitesimal increment of the chemical potential in going from the liquid to the vapor phase,

$$\begin{aligned} \delta\left(\ln \frac{x_{i'} \gamma_{i'}}{x_i \gamma_i}\right) &= \left\{\frac{\partial\left(-\frac{\mu_i^{0'} - \mu_i^0}{RT}\right)}{\partial T}\right\}_p \mathrm{d}T \\ &\quad + \left\{\frac{\partial\left(-\frac{\mu_i^0 - \mu_i^0}{RT}\right)}{\partial p}\right\}_T \mathrm{d}p \\ &= \frac{\Delta_v H_i^0}{RT^2} \mathrm{d}T - \frac{\Delta_v V_i^0}{RT} \mathrm{d}p, \end{aligned} \tag{12}$$

since

$$\left\{\frac{\partial(\mu_i/T)}{\partial T}\right\}_p = -\frac{H_i}{T^2} \tag{13}$$

and

$$\left(\frac{\partial \mu_i}{\partial p}\right)_T = V_i. \tag{14}$$

Here, $\Delta_v H_i^0$ is the molar heat of vaporization and $\Delta_v V_i^0$ the molar volume change of vaporization of ith pure component. We integrate the equation from an initial state T_i^0, p_i^0, $x_i^0 = 1$, $x_i^{0'} = 1$, $\gamma_i^0 = 1$, $\gamma_i^{0'} = 1$, corresponding to the vapor-liquid equilibrium of the pure component i, to a final equilibrium state (azeotropic point) T^a, p^a, x_i, $x_{i'}$, γ_i, $\gamma_{i'}$, so that

$$\ln \frac{x_{i'} \gamma_{i'}}{x_i \gamma_i} = \int_{T_i^0}^{T^a} \frac{\Delta_v H_i^0}{RT^2} \mathrm{d}T - \frac{1}{RT} \int_{p_i^0}^{p^a} \Delta_v V_i^0 \mathrm{d}p. \tag{15}$$

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[5] J. H. Hildebrand and R. L. Scott, "The Solubility of Non-electrolytes", Reinhold (1950), 121.

[6] I. Prigogine and R. Defay, op. cit., chapt. XVIII.

An azeotrope is formed when, in a closed system, the mass of one of the phases increases at the expense of the others without changing the composition. When the equilibrium is attained from, the definition of azeotrope formation, we have a condition as follows:

$$x_i = x_{i'}. \tag{16}$$

At a constant pressure (1 atm.) we have to consider only the first term of the right hand of equation (15). For most practical cases, it is sufficiently accurate to assume the heat of vaporization to be independent of temperature in the range considered and the vapor to be perfact ($\gamma_{i'}=1$), so we have

$$\ln \gamma_i = \frac{\Delta_v H_i^0}{RT_i^0}\frac{T_i^0 - T^a}{T^a} = \frac{\Delta_v S_i^0}{R}\frac{T_i^0 - T^a}{T^a}, \tag{17}$$

where $\Delta_v S_i^0$ is the molar entropy of vaporization of ith pure component. At a constant temperature T^a, we have, again taking the vapor to be perfect and neglecting the liquid volume compared with vapor one $\Delta_v V_i^0 = V_i^{0\prime} - V_i^0 \simeq V_i^{0\prime} \simeq RT^a/p$),

$$\gamma_i = p^a / p_i^0. \tag{18}$$

Thus we can combine equations (17) and (18) with (7) and (8) at the azeotropic point to obtain final equations for the azeotropic mixture.

At constant pressure ($p=1$ atm.) we have

$$\Delta_v S_1^0 (T_1^0 - T^a) = Nwx_2^2, \tag{19}$$

and
$$\Delta_v S_2^0 (T_2^0 - T^a) = Nwx_1^2. \tag{20}$$

At constant temperature T^a we have

$$RT^a \ln (p^a/p_1^0) = Nwx_2^2, \tag{21}$$

and
$$RT^a \ln (p^a/p_2^0) = Nwx_1^2. \tag{22}$$

Entirely the same equations as those from (19) to (22) can be derived from the final equations given by Prigogine[7] except that he has not retained Nw (α in his equations in an explicit form (2) in his further discussion of azeotropic mixtures. In the following discussion we will mainly use the equations (19) and (20), since most of the azeotropic data are investigated under constant pressure (1 atm.).

Here, it should be mentioned that if we take higher terms in the quasi-chemical treatment, we have, instead of equations (19) and (20),

$$\Delta_v S_1^0 (T_1^0 - T^a) = Nwx_2^2 \left\{ 1 + \frac{2x_1(x_1 - x_2)}{2\,!}\left(\frac{2w}{zkT^a}\right) + \frac{2x_1(x_1-x_2)(1-6x_2+6x_2^2)}{3\,!}\left(\frac{2w}{zkT^a}\right)^2 + \cdots \right\} \tag{23}$$

and

$$\Delta_v S_2^0 (T_2^0 - T^a) = Nwx_1^2 \left\{ 1 - \frac{2x_2(x_1 - x_2)}{2\,!}\left(\frac{2w}{zkT^a}\right) - \frac{2x_2(x_1-x_2)(1-6x_2+6x_2^2)}{3\,!}\left(\frac{2w}{zkT^a}\right)^2 - \cdots \right\}, \tag{24}$$

where k is Boltzmann's constant.

In the quasi-chemical approximation[8] w/kT cannot for example, exceed 2.301 for a body-centered cubic lattice, $z=8$, or 2.188 for a face-centered cubic lattice, $z=12$, without phase separation. Thus within the range $1 > x_2 \geq \frac{1}{2}$ in (23) and the range $1 > x_1 \geq \frac{1}{2}$ in (24), even the second term of the series cannot exceed 0.072 or 0.046 for the respective lattice, the higher terms being much smaller. Therefore, as far as we take the data from these ranges or their vicinity it will be sufficiently accurate to leave only the first terms as we did, but as x_2 approaches 0 in (23) and x_1 approaches 0 in (24) the error of the above approximation will be considerable. As the first step, however, we will start with the approximate equations (19) and (20) to compare the azeotrope-forming power of a number of azeotropic mixtures.

Azeotrope-forming Power and Condition for Azeotrope Formation

It is of interest for our purpose to see whether an azeotrope is of a maximum or minimum type according to the sign of w, and how the magnitude of w determines the range of boiling points or vapor pressures of pure components allowable in azeotrope formation.

If w is positive in sign we have the minimum azeotrope with $T_1^0, T_2^0 > T^a$ from equations (19) and (20) or positive azeotrope with $p^a > p_1^0, p_2^0$ from equation (21) and (22). If w is negative we have the maximum azeotrope with $T_1^0, T_2^0 < T^a$ or negative azeotrope with $p^a < p_1^0, p_2^0$ conversely.

For an azeotrope to have existence in homogeneous solution, x_i must lie between 0 and 1. Therefore as conditions of azeotrope existence we can readily derive from equations (19) and (20) or (21) and (22),

$$-\frac{Nw}{\Delta_v S_2^0} \leq T_1^0 - T_2^0 \leq \frac{Nw}{\Delta_v S_1^0} \tag{25}$$

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[7] I. Prigogine and R. Defay op. cit., p. 455 (28.25), (28.22).

[8] E. A. Guggenheim, op. cit., p. 41.

or
$$-\frac{Nw}{RT^a}\leq \ln(P_1^0/P_2^0)\leq\frac{Nw}{RT^a} \tag{26}$$
respectively.

Equation (26) is also derived by Prigogine⁹⁾. The equality in equation (25) will give maximum and minimum boiling temperatures of pure component 1. Between these temperatures various kinds of component 1 are allowed to form azeotropes with a fixed component 2. Thus w is considered as a measure of the azeotropeforming power of solutions. The larger the value of w, the more different boiling points the component 1 and 2 can have in azeotrope formation.

Discussion

For the discussion of various kinds of azeotropic mixtures it is appropriate to group them into four classes* as shown in Tables I–IV, according to the following different types of intermolecular forces: (1) force between non-polar molecules (dispersion effect): (2) force between permanent dipoles (dipole-dipole interaction): (3) force between a permanent dipole and an induced dipole (dipole-induced dipole interaction). For simplicity, we will involve in the type (2) the attraction due to hydrogen bonding that is essentially electrostatic. Among these types the second appears to have the most important effect on azeotrope formation.

(a) Dispersion Force Solutions

London¹⁰⁾ derived for the absolute value of an attractive potential between 1 and 2 molecule

$$\epsilon_{12}=-\frac{3\alpha_1\alpha_2}{2r_{12}^6}\,\frac{h\nu_{01}\cdot h\nu_{02}}{h\nu_{01}+h\nu_{02}}, \tag{27}$$

where h is Planck's constant, α_i the polarizability of the ith molecule and $h\nu_{0i}$ is the energy closely related to the ionization potential of the i-th molecule. In the model under consideration the distances between all molecules may be taken as nearly equal:

$$r_{11}=r_{12}=r_{22}=r.$$

Equations (2) and (27) can now be used to obtain

$$w=\frac{3}{2}\,\frac{z}{2}\,\frac{h}{r^6}\left\{\frac{\nu_{01}\alpha_1^2}{2}+\frac{\nu_{02}\alpha_2^2}{2}-2\frac{\nu_{01}\cdot\nu_{02}}{\nu_{01}+\nu_{02}}\alpha_1\alpha_2\right\}.$$

Noting that

$$\frac{\nu_{01}\cdot\nu_{02}}{\nu_{01}+\nu_{02}}\leq\frac{\sqrt{\nu_{01}\cdot\nu_{02}}}{2},$$

we conclude that

$$w\geq\frac{3}{2}\,\frac{z}{2}\,\frac{h}{r^6}\left\{\frac{\nu_{01}\alpha_1^2}{2}+\frac{\nu_{02}\alpha_2^2}{2}-\sqrt{\nu_{01}\cdot\nu_{02}}\,\alpha_1\alpha_2\right\}. \tag{28}$$

Thus we see that if the interactions are caused solely by dispersion force we must always have

$$w\geq 0$$

and so azeotropes, if any, are always minimum. Examples are found in azeotropes between two different types of hydrocarbons, i. e. aromatics-paraffins and aromatics-naphthens. Another examples are azeotropes between non-polar liquids and paraffinic or naphthenic hydrocarbons. Some of them (No. 1 to 5 for the former, 6 for the latter examples) are listed in Table I together with their calculated w values. Here we see that values of w calculated from equation (19) or (20) show agreement as a whole.

(b) Solutions Involving Addition Compounds

We shall have an "addition compound" in a case where the potential energies ε_{11} and ε_{22} are of the same order of magnitude, while,

$$\varepsilon_{12}\gg\varepsilon_{11},\ \ \varepsilon_{22},$$

and so

$$w<0.$$

We thus have maximum type azeotropes in this case. It appears reasonable to attribute these intermolecular forces mainly to the dipole interaction due to hydrogen bonding between components 1 and 2, but here we will not proceed further to the quantitative discussion as in the case of free molecules because of the inapplicability of simple Boltzmann's statistics. A number of instances are found in azeotropes between polyhalogen compounds and the compounds involving donor atoms such as esters, ketones, aldehydes, ethers and acetals. Examples are listed in Table II.

(c) Solutions Involving Associations in Non-polar Solvents

In this class ε_{22} is far more important than ε_{11} and ε_{12}, where ε_{22} is considered to be due mainly to dipole-dipole, ε_{11} to dispersion effect and ε_{12} to dipole-induced dipole interactions. The ε_{22} is frequently due to strong hydrogen bonding. That is,

$$\varepsilon_{22}\gg\varepsilon_{12}>\varepsilon_{11}$$

and so

$$w>0.$$

We thus have minimum type azeotropes. Examples are listed in Table III.

(d) Solutions Involving Associations in Polar Solvents

In a way similar to class (c) ε_{22} is greater

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9) I. Prigogine and R. Defay, op. cit., p. 465 (28.50).

* Similar classification was given by I. Prigogine and R. Defay, op. cit., p. 385ff.

10) F. London, *Trans. Faraday Soc.*, 33, 19 (1937), *J. Phys. Chem.*, 46, 305 (1942).

than ε_{12} or ε_{11}, but the differences between them are not so great as in class (c), the difference between ε_{11} and ε_{12} being smaller than that between ε_{22} and ε_{12}:

$$\varepsilon_{22}>\varepsilon_{12},\ \varepsilon_{22}>\varepsilon_{11},\ (\varepsilon_{22}-\varepsilon_{12})>\ \varepsilon_{11}-\varepsilon_{12}\ ,$$

so still we have

$$w>0.$$

Here all ε's are considered to be due to a certain extent to dipole interaction (or hydrogen bonding). Thus azeotropes are minimum, but their extents are not so great as in the class (c), with a few exceptions. Examples are given in Table IV.

TABLE I

AZEOTROPIC DATA OF CLASS (a)

No.	Component 2	Component 1	T_2^0 (°C)	T_1^0 (°C)	T^a (°C)	x_2 a) (mole fraction)	$\Delta_v S_1^{0b)}$ $\left(\frac{\text{cal}}{M°\text{C}}\right)$	$\Delta_v S_1^{0b)}$ $\left(\frac{\text{cal}}{M°\text{C}}\right)$	Nw_1 $\left(\frac{\text{kcal}}{M}\right)$	Nw_2 $\left(\frac{\text{kcal}}{M}\right)$
1	Benzene	2,2-Dimethylpentane	80.15	79.1	75.85	0.526	(20.3)	20.8	0.24	0.40
2	Benzene	2,4-Dimethylpentane	80.15	80.8	76.7	0.536	(20.3)	20.8	0.40	0.48
3	Benzene	Cyclohexane	80.15	80.6	77.7	0.537	20.4	20.8	0.20	0.24
4	Toluene	2,3,4-Trimethylpentane	110.7	113.5	109.5	0.615	(20.3)	20.8	0.19	0.20
5	Toluene	*cis-trans-cis*-1,2,4-trimethylcyclopentene	110.7	109.3	107.4	0.439	(20.3)	20.8	0.24	0.24
6	Carbon disulfide	Cyclopentane	46.25	49.4	44.0	0.652	(20.3)	20.0	0.25	0.37

Azeotropic data are taken from Horsely's "Azeotropic Data" published in 1956 by the American Chemical Society except for butanethiol (R. L. Denyer, F. A. Fidler and R. A. Lowry, *Ind. Eng Chem.*, **41**, 2727 (1949).

a) Mole fractions calculated from wt. % in Horsely's data.

b) Values taken from "International Critical Table", Vol. V (1929).

Values enclosed in parentheses are those presumed from similar substances.

TABLE II

AZEOTROPIC DATA OF CLASS (b)

No.	Component 2	Component 1	T_2^0 (°C)	T_1^0 (°C)	T^a (°C)	x_2 a) (mole fraction)	$\Delta_v S_1^{0b)}$ $\left(\frac{\text{cal}}{M°\text{C}}\right)$	$\Delta_v S_2^{0b)}$ $\left(\frac{\text{cal}}{M°\text{C}}\right)$	Nw_1 $\left(\frac{\text{kcal}}{M}\right)$	Nw_2 $\left(\frac{\text{kcal}}{M}\right)$
1	Trichloromethane	2-Propanone	61.2	56.10	64.43	0.640	22.0	21.0	−0.45	−0.52
2	Bromodichloromethane	2-Butanone	90.2	79.6	90.85	0.790	21.7	(21.0)	−0.39	−0.31
3	Bromodichloromethane	3-Methyl-2--butanone	90.2	95.4	97.2	0.348	(21.0)	(21.0)	−0.31	−0.35
4	Bromodichloromethane	Propyl Ethanonate	90.2	101.6	102.3	0.207	21.9	(21.0)	−0.36	−0.40
5	Bromodichloromethane	Methyl Carbonate	90.2	90.35	91.95	0.499	21.8	(21.0)	−0.14	−0.15
6	Trichloroethylene	Diethoxymethane	86.9	87.9	89.2	0.477	(21.7)	21.0	−0.12	−0.18

TABLE III

AZEOTROPIC DATA OF CLASS (c)

No.	Component 2	Component 1	T_2^0 (°C)	T_1^0 (°C)	T^a (°C)	x_2 a) (mole fraction)	$\Delta_v S_1^{0b)}$ $\left(\frac{\text{cal}}{M°\text{C}}\right)$	$\Delta_v S_2^{0b)}$ $\left(\frac{\text{cal}}{M°\text{C}}\right)$	Nw_1 $\left(\frac{\text{kcal}}{M}\right)$	Nw_2 $\left(\frac{\text{kcal}}{M}\right)$
1	Trichloromethane	2,3-Dimethylbutane	61.2	58.0	55.5	0.391	(20.3)	21.0	0.33	0.32
2	Acetonitrile	Carbon tetrachloride	81.6	76.75	75.3	0.434	20.4	20.2	1.26	1.04
3	Acetonitrile	Benzene	81.6	80.1	73	0.494	20.8	20.2	0.61	0.68
4	Nitromethane	Toluene	101.2	110.75	96.5	0.648	20.8	22.1	0.71	0.84

No.	Component 2	Component 1	T_2^0 (°C)	T_1^0 (°C)	T^a (°C)	x_2 a) (mole fraction)	$\Delta_v S_1^{0b)}$ $\left(\frac{\text{cal}}{M°\text{C}}\right)$	$\Delta_v S_1^{0b)}$ $\left(\frac{\text{cal}}{M°\text{C}}\right)$	Nw_1 $\left(\frac{\text{kcal}}{M}\right)$	Nw_2 $\left(\frac{\text{kcal}}{M}\right)$
5	Nitromethane	Cyclohexane	101.2	80.75	70.2	0.349	20.4	22.1	1.76	1.62
6	Nitromethane	Heptane	101.2	98.4	80.2	0.492	20.6	22.1	1.55	1.79
7	Butanethiol	Heptane	98.58	98.40	95.45	0.520	20.6	(23.4)	0.23	0.32
8	Butanethiol	Methylcyclohexane	98.58	101.05	97.0	0.603	20.2	(23.4)	0.22	0.23
9	Phenol	Indene	182.2	183.0	177.8	0.523	(20.3)	(22)	0.39	0.43
10	1,2-Benzenediol	2-Methylnaphthalene	245.9	241.15	233.25	0.431	(20.3)	(22.5)	0.86	0.88
11	1,3-Benzenediol	2-Methylnaphthalene	281.4	241.15	240.05	0.131	(20.3)	(23.5)	1.30	1.29

Table IV

Azeotropic data of class (d)

No.	Component 2	Component 1	T_2^0 (°C)	T_1^0 (°C)	T^a (°C)	x_2 a) (mole fraction)	$\Delta_v S_1^{0b)}$ $\left(\frac{\text{cal}}{M°\text{C}}\right)$	$\Delta_v S_2^{0b)}$ $\left(\frac{\text{cal}}{M°\text{C}}\right)$	Nw_1 $\left(\frac{\text{kcal}}{M}\right)$	Nw_2 $\left(\frac{\text{kcal}}{M}\right)$
1	Acetonitrile	Methyl Propanoate	81.6	79.85	76.2	0.479	21.9	20.2	0.35	0.40
2	Acetonitrile	Propyl methanoate	81.6	80.85	76.5	0.513	22.0	20.2	0.36	0.44
3	Acetonitrile	1-Chlorobutane	81.6	78.5	67.2	0.526	(20.7)	20.2	0.85	1.29
4	Acetonitrile	1-Chloro-2-methylpropane	81.6	68.85	62.0	0.360	(20.7)	20.2	1.09	0.97
5	Nitromethane	1-Bromobutane	101.2	101.5	90.0	0.691	(20.7)	22.1	0.50	2.60
6	Nitromethane	1-Bromo-2-methylpropane	101.2	91.4	84.0	0.536	(20.7)	22.1	0.53	1.77
7	Nitromethane	2-Iodopropane	101.2	89.45	82.0	0.579	(20.7)	22.1	0.46	2.40
8	Nitromethane	2-Pentanone	101.2	102.35	99.15	0.643	(21)	22.1	0.16	0.36
9	Nitromethane	3-Pentanone	101.2	102.05	99.1	0.633	20.9	22.1	0.16	0.34
10	Nitromethane	Ethyl Propanoate	101.2	99.1	96.0	0.474	22.0	22.1	0.31	0.42
11	Nitromethane	Methyl Butanoate	101.2	102.65	97.95	0.627	21.7	22.1	0.26	0.52
12	Nitromethane	Propyl Ethanoate	101.2	101.6	97.6	0.578	21.9	22.1	0.26	0.45
13	1,2-Benzendiol	1,4-Dibromobenzene	245.9	220.25	218.15	0.192	(21.3)	(22.5)	1.21	0.96
14	1,2-Benzendiol	1-Chloronaphthalene	245.9	262.7	241.0	0.680	(21.3)	(22.5)	1.00	1.08

In the above classifications all ε's in each type of solution of course involve more or less attractive energy due to dispersion effect.

So far we have considered the azeotropic mixtures on the basis of the fairly simple model proposed. Apparently it is not satisfactory for quantitative discussions, since the values of w_1 and w_2 calculated from equations (19) and (20), respectively, do not agree so well with each other, though they show rough coincidences. The cause of considerable disagreements in No. 1 and 6 of Table I is uncertain and will be left to further study. It is mentioned, however, that this disagreement may be partly due to the approximation we used on the one hand and to the errors introduced in experimental data on the other hand. In the class (d) solution such a disagreement is remarkable and in most cases $w_1 < w_2$. This will give a measure of the deviation of activity coefficients from regular solutions.

It is of great interest to see how w's change with varying pairs of component molecules in connection with the azeotrope-forming power of solutions. In general the decreasing order of azeotrope-forming power are (c), (d), (a) in minimum type azeotropes.

Summary

The general expression for the azeotrope-forming power of binary solution has been derived and the conditions for azeotrope existence presented. The quasi-crystalline model has been adopted for the solution, which is assumed to be a strictly regular solution at an azetropic point and an explicit representation for interaction energy of component molecules introduced.

Azeotropic mixtures have been grouped into four classes according to the type of molecular interaction and the azeotrope-forming power (molecular interchange energy) has been calculated and discussed.

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