A RELATION BETWEEN EXCESS VOLUME AND THE FORM OF THE DEPENDENCE OF DENSITY ON COMPOSITION FOR BINARY LIQUID MIXTURES

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A relation of excess volume and density is analyzed for binary liquid mixtures. It is shown that, unlike the ideal mixture, whose density is a monotonous function of composition, extremes may appear on the density curves of mixtures with non-zero excess volumes. Conditions for the existence of extremes are derived. Some examples are also given and briefly discussed.

Density and excess volume (volume change on mixing) are two quantities of mixtures that are closely related. While the concentration dependence of density is well-defined for the ideal mixture, a nonideality, represented by excess volume, may change it significantly in such a way that the density curves quite different from that for the ideal mixture may be observed for real mixtures. In this paper, characteristic features of the ideal mixture are briefly summarized and several cases when extremes may occur on the density curves of real mixtures are discussed. To minimize a number of possible cases to be analyzed, components are numbered in such a way that the inequality $\varrho_1 \geqq \varrho_2$ holds throughout this paper. Mole fraction of component 2, $x_2 = 1 - x_1$, is regarded as an independent variable.

Density and excess volume are related in terms of the formula

$$\varrho(x_2) = \frac{M}{V} = \frac{(1 - x_2) M_1 + x_2 M_2}{(1 - x_2) V_1^0 + x_2 V_2^0 + V^E(x_2)} = \frac{(1 - x_2) M_1 + x_2 M_2}{[(1 - x_2) M_1]/\varrho_1 + (x_2 M_2/\varrho_2) + V^E(x_2)}, \quad (1)$$

where M and V are the molar mass and molar volume of a mixture, M_i, V_i^0, ϱ_i ($i = 1, 2$) are the molar masses, molar volumes and densities of pure components, respectively, and V^E is the molar excess volume. As it can be easily derived, the derivative of function (*1*) is given by

$$\frac{d\varrho}{dx_2} = \frac{M_1 M_2}{V^2}\left(\frac{1}{\varrho_1} - \frac{1}{\varrho_2}\right) + \frac{(M_2 - M_1) V^E - M(dV^E/dx_2)}{V^2}. \quad (2)$$

Ideal Mixture

One of the characteristic features of ideal mixture is that an isothermal isobaric mixing is accompanied by no volume change, i.e. $V^E(x_2) = 0$ holds for all x_2. Then Eq. (*2*) simplifies into

$$\left(\frac{\mathrm{d}\varrho}{\mathrm{d}x_2}\right) = \frac{M_1 M_2}{V^2}\left(\frac{1}{\varrho_1} - \frac{1}{\varrho_2}\right). \tag{3}$$

Obviously function $\varrho(x_2)$ (Eq. (*1*) with $V^E = 0$) cannot exhibit any extreme because $(\mathrm{d}\varrho/\mathrm{d}x_2) \neq 0$ for $\varrho_1 \neq \varrho_2$. The only case when $(\mathrm{d}\varrho/\mathrm{d}x_2) = 0$ is that if $\varrho_1 = \varrho_2$ and consequently $\varrho(x_2) = \varrho_1 = \varrho_2$ holds for all $x_2 \in \langle 0, 1 \rangle$ here.

It can be derived from Eq. (*3*)

$$\left(\frac{\mathrm{d}^2\varrho}{\mathrm{d}x_2^2}\right) = 2M_1 M_2\left(\frac{1}{\varrho_1} - \frac{1}{\varrho_2}\right)\frac{V_1^0 - V_2^0}{V^3}. \tag{4}$$

It is evident that function $\varrho(x_2)$ is a straight line $((\mathrm{d}^2\varrho/\mathrm{d}x_2^2) = 0)$ either if $\varrho_1 = \varrho_2$ (which is the case discussed above) or if $V_1^0 = V_2^0$ (then $(\mathrm{d}\varrho/\mathrm{d}x_2) = \varrho_2 - \varrho_1$ follows from Eq. (*3*)). Otherwise the $\varrho(x_2)$ dependence may be either a convex curve if $V_1^0 < V_2^0$ or a concave curve if $V_1^0 > V_2^0$.

Real Mixtures

It is impossible to make a similar detailed general analysis of function $\varrho(x_2)$ for real mixtures since the nonideality represented by excess molar volume, $V^E(x_2)$, cannot be expressed by any general formula. However, some conclusions concerning the shape of function $\varrho(x_2)$ can be reached on the basis of the following considerations.

If function $\varrho(x_2)$ has an absolute maximum for a certain composition from the open interval $(0, 1)$, then there must be a subinterval of x_2 in which the inequality

$$\varrho(x_2) > \varrho_1 \tag{5}$$

holds. After introducing Eq. (*1*) into relation (*5*) and rearranging the inequality

$$V^E(x_2) < x_2 M_2\left(\frac{1}{\varrho_1} - \frac{1}{\varrho_2}\right) \tag{6}$$

results. Similarly, if function $\varrho(x_2)$ has an absolute minimum, than there must be a subinterval of x_2 in which

$$\varrho(x_2) < \varrho_2 \tag{7}$$

holds. Then

$$V^E(x_2) > (1 - x_2) M_1 \left(\frac{1}{\varrho_2} - \frac{1}{\varrho_1}\right) \tag{8}$$

follows from Eq. (*1*) and relation (7). A special case is that one if $\varrho_1 = \varrho_2$. Then the sign of excess volume determines whether a density curve exhibits a maximum(for $V^E < 0$) or a minimum (for $V^E > 0$).

Right-hand sides of inequalities (*6*) and (*8*) are straight-line functions of x_2, passing through zero for $x_2 = 0$ and $x_2 = 1$, respectively. These straight lines can be drawn into the (V^E vs x_2) plot of a particular mixture to determine the respective composition intervals. Schematical illustration is shown in Fig. 1 for several typical simple dependences of excess volume on mole fraction along with the corresponding density curves. Mixtures of type *IV* probably do not exist since there densities of pure components with low molar masses should be very close to each other and excess volumes large with an S-shaped composition dependence. On the other hand, experimental data for the mixtures representing type *I* can be found in the literature, for example aqueous solutions of some carboxylic acids: acetic acid[1], propionic acid[2], trifluoroacetic acid[3]. Experimental data for the other types were not found in the literature and any notice concerning data for these types of mixtures sent to the author would be greatly appreciated. It should be mentioned that, unlike types *I*–*III*, local extremes may occur on density curves of type *IV* but density at such points can lie within densities of pure components, i.e. conditions (*5*) and (*7*) may not be fulfilled.

As it follows from Fig. 1, the conditions of existence of absolute extremes on the $\varrho(x_2)$ curve of types *I*–*III* may also be expressed by means of limiting derivatives of excess volume. Inequality

$$\left(\frac{dV^E}{dx_2}\right)_{x_2 \to 0} < M_2 \left(\frac{1}{\varrho_1} - \frac{1}{\varrho_2}\right) \tag{9}$$

should hold if there is a maximum on the $\varrho(x_2)$ curve, and

$$\left(\frac{dV^E}{dx_2}\right)_{x_2 \to 1} < -M_1 \left(\frac{1}{\varrho_2} - \frac{1}{\varrho_1}\right) \tag{10}$$

if there is a minimum. Substituting inequality (*9*) into the limiting form ($x_2 \to 0$) of Eq. (*2*), the relation $(d\varrho/dx_2)_{x_2 \to 0} > 0$ can be derived. Similarly inequality (*10*) combined with Eq. (*2*) gives $(d\varrho/dx_2)_{x_2 \to 1} > 0$.

The derivatives of excess volume can be expressed in terms of partial molar volumes,

$$\bar{V}_1 = V_1^0 + V^{\mathrm{E}} - x_2 \left(\frac{\mathrm{d}V^{\mathrm{E}}}{\mathrm{d}x_2} \right) \tag{11}$$

and

$$\bar{V}_2 = V_2^0 + V^{\mathrm{E}} + (1 - x_2) \left(\frac{\mathrm{d}V^{\mathrm{E}}}{\mathrm{d}x_2} \right), \tag{12}$$

and then inequalities (*9*) and (*10*) can be rewritten into the forms

$$(\bar{V}_2)_{x_2 \to 0} < V_2^0 \varrho_2 / \varrho_1 \,, \tag{13}$$

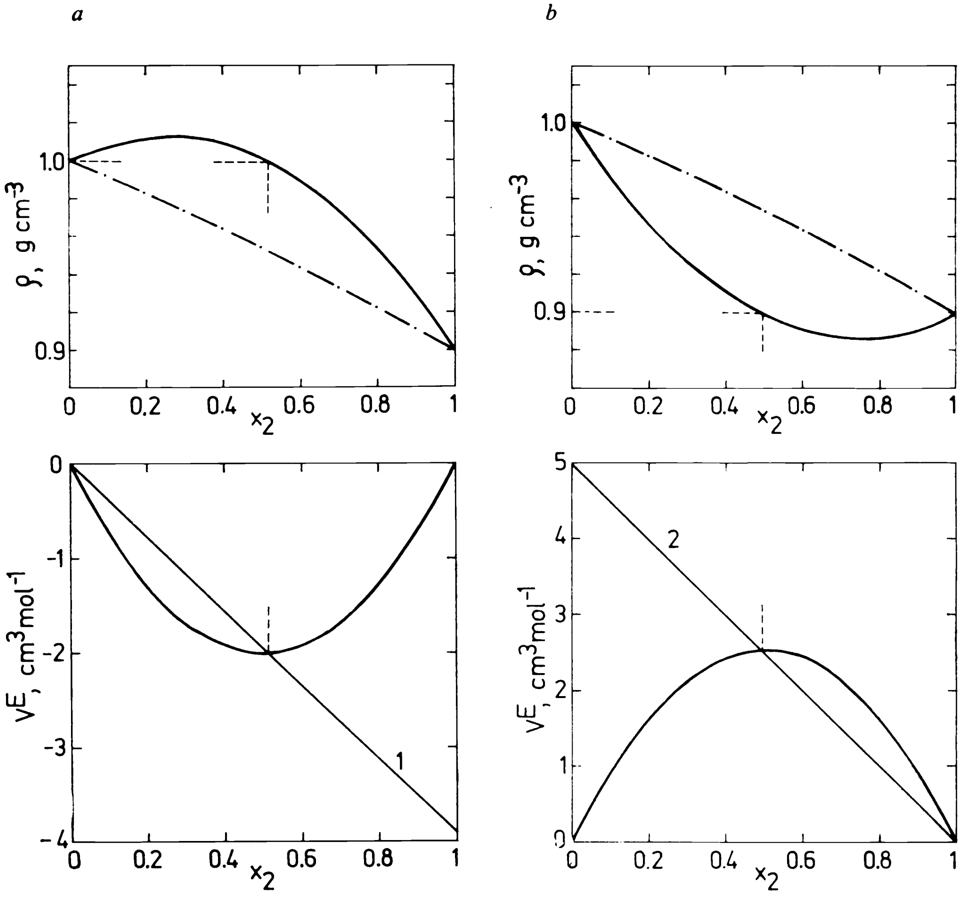


FIG. 1

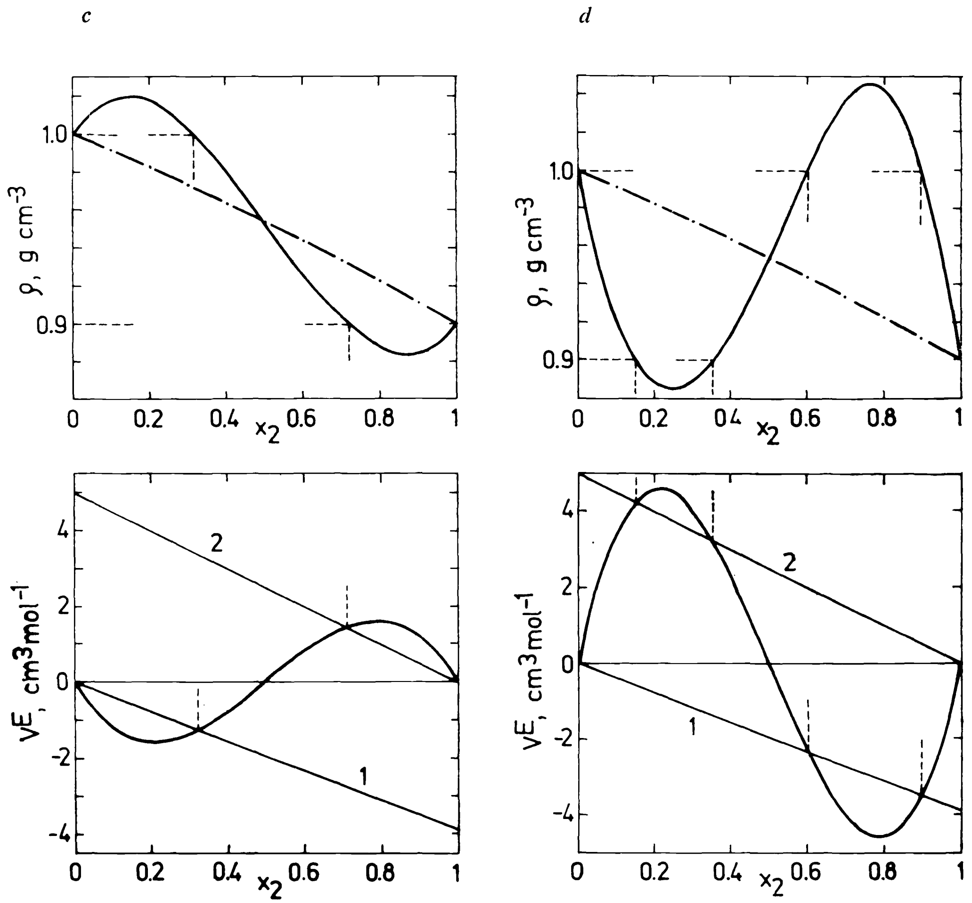
Dependences of density and excess volume on mole fraction for the model mixture with $\varrho_1 =$ $= 1\ \mathrm{g\,cm^{-3}}$, $\varrho_2 = 0{\cdot}9\ \mathrm{g\,cm^{-3}}$, $M_1 = 45\ \mathrm{g\,mol^{-1}}$, and $M_2 = 35\ \mathrm{g\,mol^{-1}}$. *a* Type *I*: $V^{\mathrm{E}} =$

that represents the condition for existence of a maximum, and

$$(\bar{V}_1)_{x_2 \to 1} > V_1^0 \varrho_1/\varrho_2 \tag{14}$$

for existence of a minimum on the $\varrho(x_2)$ curve for types *I–III*.

The conditions, as derived above, determine whether the concentration dependence of density exhibits absolute extremes or not, and allow to evaluate an interval of composition in which density of a mixture does not fall into the interval between the densities of pure components on the basis of the excess volume curve. Evaluation of the composition for which there is an extreme (including local extremes) on the



$= -8(1 - x_2)x_2$, *b* type *II*: $V^E = 10(1 - x_2)x_2$, *c* type *III*: $V^E = 16(1 - x_2)x_2(2x_2 - 1)$, *d* type *IV*: $V^E = 48(1 - x_2)x_2(1 - 2x_2)$; —·—·— density curve for ideal mixture ($V^E = 0$); straight lines: *1* $x_2M_2(1/\varrho_1 - 1/\varrho_2)$, *2* $(1 - x_2)M_1(1/\varrho_2 - 1/\varrho_1)$

density curve can be made by solving the equation

$$\left(\frac{d\varrho}{dx_2}\right) = 0\,. \qquad (15)$$

It follows from Eqs (*2*) and (*15*) that

$$\left(\frac{dV^E}{dx_2}\right) = \frac{M_2\left(\frac{1}{\varrho_1} - \frac{1}{\varrho_2}\right) + \left(\frac{M_2}{M_1} - 1\right)V^E}{1 + \left(\frac{M_2}{M_1} - 1\right)x_2}\,. \qquad (16)$$

A special case occurs if $M_1 = M_2$. Then

$$\left(\frac{dV^E}{dx_2}\right) = M_1\left(\frac{1}{\varrho_1} - \frac{1}{\varrho_2}\right) = M_2\left(\frac{1}{\varrho_1} - \frac{1}{\varrho_2}\right) \qquad (17)$$

holds. Eq. (*17*) has a simple graphical interpretation; the mole fraction, at which a tangent to the excess volume curve is parallel with the straight lines $x_2M_2(1/\varrho_1 - 1/\varrho_2)$ or $(1 - x_2)\,M_1(1/\varrho_2 - 1/\varrho_1)$ (see Fig. 1, in case of $M_1 = M_2$ both the lines are of the same slope), is the composition at which the density curve exhibits an extreme. Unfortunately, this simple case cannot be expected to be frequent; however, for mixtures of components with molar masess mutually not very different, Eq. (*17*) may serve for the estimation of position of extremes on the density curve, Of course, if the $V^E(x_2)$ function in an analytical form is available[4], then Eq. (*16*) can be solved exactly.

The analysis, as performed above, shows that a departure from ideality may dramatically change the form of the concentration dependence of density compared to the ideal mixture. There are many experimental data on excess volume published in the literature that allow to make an analysis for a particular mixture. Quantitative information on excess volumes of a large number of binary liquid mixtures were collected by Handa and Benson[4], some other reviews[5,6] present bibliographies on the excess volume data.

As it has been shown, in some cases even extremes can appear on the density curve and values of density are not necessarily within the range of densities of pure components. This fact may be important when the density measurements are used for the determination of composition of binary mixtures or for the verification of purity of samples of liquids being purified. In the latter case, it is usually assumed that for low concentrations of impurities, the values of excess volume are small enough that the relations valid for the ideal mixture may be employed to estimate a content of the impurity. This can lead to erroneous conclusions. For example, water as an impurity increases density of acetic acid[1] despite its density is lower than density of pure acetic acid ($\varrho = 1{\cdot}044\ \mathrm{g\,cm^{-3}}$ at 25°C). Bylicki et al.[7] have reported that the density of benzene saturated with water is lower than that of pure benzene by $0{\cdot}000154\ \mathrm{g\,cm^{-3}}$ at 25°C. Excess volume data are missing for this system (obviously because of low mutual miscibility of the components), however, large positive excess volumes, i.e. type *II* (see Fig. 1), can be expected here as the consequence of both breaking the hydrogen-bonded water aggregates and loosening the closely packed benzene structure.

REFERENCES

1. Cambell A. N., Kartzmark E. M., Gieskes G. M. T. M.: Can. J. Chem. *41*, 407 (1963).
2. Subha M. C. S., Brahmajirao S.: Indian J. Chem., A *26*, 950 (1987).
3. Fialkov J. J., Zhikharev V. S.: Zh. Obshch. Khim. *33*, 3789 (1963).
4. Handa Y. P., Benson G. C.: Fluid Phase Equilib. *3*, 185 (1979).
5. Battino R.: Chem. Revs. *71*, 5 (1971).
6. Cibulka I., Holub R.: Chem. Listy *72*, 457 (1978).
7. Bylicki A., Kozdon A., Rogalski M.: Bull. Acad. Pol. Sci., Ser. Sci. Chim. *26*, 877 (1978).

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