

A Consequence from the Model Description of a Decomposing Liquid Mixture

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Abstract—In terms of representation [1] of a decomposing binary liquid mixture as a system of two coupled self-oscillators with partial frequencies ν_A and ν_B , the following conjecture is verified: given frequency ratios ν_A/ν_B and ν_A/ν_C for decomposing liquid mixtures $A-B$ and $A-C$ at the same temperature, it is possible to determine the ν_B/ν_C ratio, which is independent of the choice of the A component.

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INTRODUCTION

In [1], a model of the boundary curve of a decomposing binary liquid mixture was proposed on the basis of the analogy between the properties of a binary mixture and a system of coupled self-oscillators. The analogy consists in the fact that both a binary decomposing mixture and a coupled self-oscillator can be found in two states each of which is similar to the respective state of the other system. One of the states corresponds to coexistence of two phases which are fairly autonomous but interacting to a certain extent. In the other state, these two parts behave as a consistent whole. In case of self-oscillating systems, the first state is known as a biharmonic mode, in which each of two self-oscillating system performs quasi-harmonic oscillations at its own frequency close to the partial one. In the case of binary liquid mixtures, the first state is represented by a two-phase region on the phase diagram and the mixture behaves as a system decomposing into two layers. The second state for a system of self-oscillators corresponds to a synchronous oscillation mode, in which both coupled systems oscillate at the same frequency close to the eigenfrequency of the oscillator with higher amplitude. For binary liquid mixtures, the state in which both parts behave as a single whole is the state of complete dissolution. The mixture becomes monophase if the amount of one component (measured, for example, in moles) significantly exceeds the amount of the other component. In [1], it is proposed that the boundary curve separating the monophase region from the binary one can be described using the mathematical apparatus elaborated in the theory of self-oscillating systems [2]. Specifically, the equations that are valid near the boundary of the domain of synchronism are applied. These equations relate the amplitudes of self-oscillators,

their partial frequencies, and coupling factors. The resulting boundary curve appears in the analytical form

$$\left(\frac{\nu_a}{\nu_b}\right)^2 = \frac{1 - \alpha_1(1 - x_a)/x_a}{1 - \alpha_2 x_a/(1 - x_a)}, \quad (1)$$

which describes the ratio of partial frequencies ν_a/ν_b as a function of mole concentration x_a , where ν_a and ν_b are effective frequencies assigned to the pure A and B components. These frequencies are assumed to be one-to-one functions of temperature. Quantities α_1 and α_2 are dimensionless coupling factors.

The boundary curve in terms of variables ν_a/ν_b and x_a is a transform of a real boundary curve usually written in terms of T and x_a . Physically, the use of the self-oscillation model is substantiated by the fact that the thermal motion of molecules is a self-oscillation process to a certain extent. Before mixing, pure components are evidently characterized by different spectra of thermal motion. After being mixed under the conditions of complete solubility, the phases become indiscernible and, therefore, their thermal spectra may be considered to be equal. In [1], the notion of spectra is replaced by effective frequencies ν_a and ν_b . Formula (1) should be considered as semiempirical, since no method for independent determination of frequencies ν_a and ν_b is yet specified.

In this study, we consider the possibility of verifying one of the consequences following from the model of a decomposing binary liquid system proposed in [1]. Note that the systems dealt with in [1] had only the lower critical decomposition point. For comprehensiveness sake, let us construct another example of a boundary curve for a system also having an upper critical decomposition point.

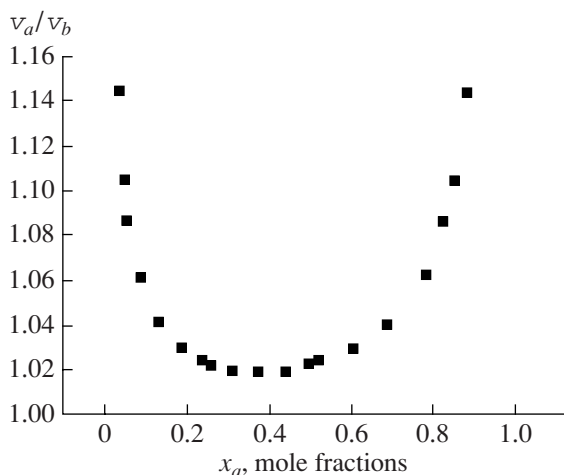


Fig. 1. Boundary curve for the perfluorodecalin–heptane system in the $(x_a, v_a/v_b)$ coordinates. Perfluorodecalin is the a component.

MODEL CALCULATION OF A BOUNDARY CURVE WITH THE UPPER CRITICAL POINT

Consider a perfluorodecalin–heptane system. For this system, there are experimental data [3] of concentrations at the left (x_a) and right (x'_a) branches of the boundary curve at the same values of temperature. Our aim is to determine the coupling factors α_1 and α_2 . They can be found from Eq. (1), more precisely, from a system of two equations. Indeed, in the temperature range below the critical point of decomposition, each temperature value corresponds to two values of concentration, x_a and x'_a . Since the frequency ratio v_a/v_b is a one-to-

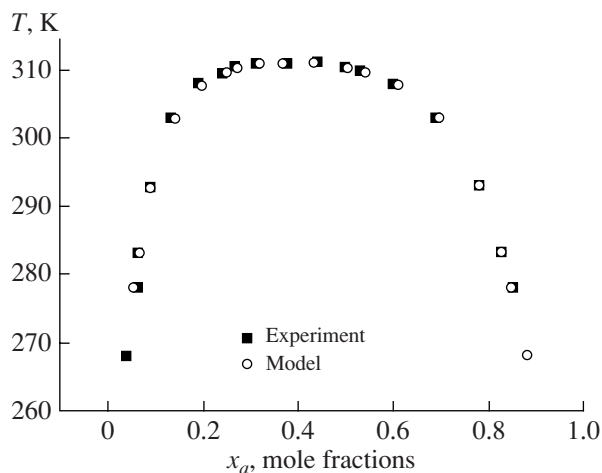


Fig. 2. Boundary curve for the perfluorodecalin–heptane system: experimental data [3] and the right (left) branch reconstructed from the data for the left (right) branch.

one function of temperature, there are also two values of concentration corresponding to each value of this ratio. Therefore, Eq. (1) can be written twice for each value of v_a/v_b : with the use of x_a and x'_a . Elimination of v_a/v_b yields an equation relating x_a and x'_a . If there are two pairs of anchor points corresponding to two values of temperature T_1 and T_2 , we obtain a system of two equations and solve it for α_1 and α_2 . In case of the perfluorodecalin–heptane system, $\alpha_1 = -0.0118$ and $\alpha_2 = 0.0312$. Then, using (1), we express the mole concentration x_a in terms of the frequency ratio v_a/v_b :

$$x_a = \frac{1 - (v_a/v_b)^2 + 2\alpha_1 \pm [(1 - (v_a/v_b)^2)^2 + 4\alpha_1\alpha_2(v_a/v_b)^2]^{1/2}}{2[1 - (1 + \alpha_2)(v_a/v_b)^2 + \alpha_1]} \quad (2)$$

Formula (2) describes the boundary curve in terms of the concentration and the v_a/v_b ratio. Such a curve should fit an experimental decomposition curve (of perfluorodecalin–heptane in our case). By setting the radicand in (2) to zero, we estimate the critical frequency ratio $(v_a/v_b)_{cr}$ at 1.01937. From formula (2), critical concentration x_{cr} was determined to be 0.3763. The corresponding value obtained in [3] is 0.3736. Using formula (1), it is possible to reconstruct the concentrations at the right branch of the boundary curve from concentrations at the left branch. Figure 1 shows a transform of the curve of phase coexistence in the perfluorodecalin–heptane system in coordinates x_a and v_a/v_b . Figure 2 plots the experimental boundary curve (black squares) along with the reconstructions (circles) of the right (left) branch from the experimental data for the

left (right) branch. It is seen that the results of experiment and calculation agree fairly well.

THE POSSIBILITY OF PREDICTING THE FREQUENCY RATIO IN THE ABSENCE OF EXPERIMENTAL DATA

In [1], the important suggestion is made that partial frequencies v_a and v_b are one-to-one functions of temperature. It follows from this assumption that, given a system $A-B$ with known ratio v_A/v_B and a system $A-C$ with ratio v_A/v_C known at the same temperature, one can determine the ratio v_B/v_C at this temperature. If this ratio can also be determined from a combination of other systems, for example, $D-B$ and $D-C$, the values of v_B/v_C found from different combinations must coincide (of course, all the frequency ratios should be taken

Table 1. Experimental concentrations at the boundary curves in the mixtures of fluorine substituted alkanes with alcohols [3] in the temperature range from 288.16 to 318.16 K

<i>T</i> , K	C ₆ F ₁₄ -C ₃ H ₇ OH		C ₆ F ₁₄ -C ₄ H ₉ OH		C ₆ F ₁₄ -C ₆ H ₁₃ OH	
	<i>x_a</i>	<i>x'_a</i>	<i>x_a</i>	<i>x'_a</i>	<i>x_a</i>	<i>x'_a</i>
288.16	0.0045	0.9956	0.005	0.9967	0.0054	0.998
298.16	0.0052	0.9912	0.0059	0.9944	0.0063	0.9965
308.16	0.0063	0.9865	0.007	0.9901	0.0076	0.9943
318.16	0.0072	0.9823	0.008	0.9878	0.009	0.9925
<i>T</i> , K	C ₇ F ₁₆ -C ₃ H ₇ OH		C ₇ F ₁₆ -C ₄ H ₉ OH		C ₇ F ₁₆ -C ₆ H ₁₃ OH	
	<i>x_a</i>	<i>x'_a</i>	<i>x_a</i>	<i>x'_a</i>	<i>x_a</i>	<i>x'_a</i>
288.16	0.0027	0.9957	0.0029	0.9968	0.003	0.9979
298.16	0.0034	0.9917	0.0035	0.9948	0.0037	0.9966
308.16	0.0039	0.9871	0.0044	0.989	0.0043	0.9945
318.16	0.0046	0.984	0.0051	0.9861	0.0057	0.9928

Table 2. Calculated critical values of the frequency ratios and mole concentrations

	C ₆ F ₁₄ -C ₃ H ₇ OH	C ₆ F ₁₄ -C ₄ H ₉ OH	C ₆ F ₁₄ -C ₆ H ₁₃ OH
(<i>v_A/v_B</i>) _{cr}	0.9918	0.9927	0.9945
<i>x_{cr}</i>	0.3088	0.3566	0.4374
	C ₇ F ₁₆ -C ₃ H ₇ OH	C ₇ F ₁₆ -C ₄ H ₉ OH	C ₇ F ₁₆ -C ₆ H ₁₃ OH
(<i>v_A/v_B</i>) _{cr}	0.9943	0.9948	0.9964
<i>x_{cr}</i>	0.272	0.3052	0.3829

at the same temperature). It seemed important to check this conjecture. The basic difficulty in doing this was to find at least four systems with the necessary data known at equal temperatures. Such data were found in study [4], where portions of the boundary curves were obtained experimentally for systems including fluorine-substituted alkanes and monohydric alcohols at four values of temperature. Some data borrowed from [4] are reproduced in Table 1.

A number of special features of the binary systems studied in [4] should be noted. The data presented in [4] refer to only a narrow temperature interval from 288 to 318 K, which is far from the critical points of decomposition for the studied systems. This can be inferred from the fact that the mole concentrations are very close to zero at the points related to the left branch and are very close to unity at the points related to the right branch (for example, for the C₆F₁₄-C₃H₇OH system, the mole concentrations are $x_{C_6F_{14}} = 0.0045$ and $x'_{C_6F_{14}} = 0.9956$ at 288 K). No critical parameters are mentioned in [4]. Probably, the critical points cannot be achieved in these systems. To clarify this point requires estimating the critical concentrations, for example, using the scheme proposed in [1] and briefly outlined above. For all the

systems in question, the anchor points were taken at temperatures $T_1 = 288.16$ K and $T_2 = 308$ K. The concentrations corresponding to these temperatures in each of the binary systems are given in Table 1. The coupling factors were determined using Eq. (1) in accordance with the procedure described above. The calculated values of critical concentrations x_{cr} and critical frequency ratios are listed in Table 2. Remarkably, all the critical ratios between the frequencies of perfluoroalkanes and alcohols are close to unity. This is due to the small coupling factors, on the order of 10^{-3} , obtained for these systems. Table 3 presents the calculated ratios v_A/v_B , where *A* is a perfluoroalkane and *B* is an alkanol (third and fourth columns). Taking the ratios between the frequencies of perfluorohexane and an alcohol and between the frequencies of perfluoroheptane and the frequency of the same alcohol from Table 3, one can derive the ratio between the perfluorohexane and perfluoroheptane frequencies. For example, if $v_{C_6F_{14}}/v_{C_3H_7OH} = 0.4382$ and $v_{C_7F_{16}}/v_{C_3H_7OH} = 0.4697$ at 288.16 K, the resulting ratio $v_{C_6F_{14}}/v_{C_7F_{16}} = 0.93283$. The fifth column of Table 3 lists the values of this ratio as derived for the mixtures of perfluorohexane and perfluoroheptane with three types of alcohols at different

Table 3. Ratios between the perfluorohexane and perfluoroheptane frequencies obtained from the ratios between each of these frequencies and the frequency of the alcohol

T, K	Perfluoroalkane → alkanol ↓	C_6F_{14} frequency ratio	C_7F_{16} frequency ratio	$\nu_{C_6F_{14}}/\nu_{C_7F_{16}}$	$(\nu_{C_6F_{14}}/\nu_{C_7F_{16}})_{avg}$
288.16	C_3H_7OH	0.4382	0.4697	0.9328	0.9494
	C_4H_9OH	0.4472	0.4611	0.9699	
	$C_6H_{13}OH$	0.4700	0.5170	0.9090	
298.16	C_3H_7OH	0.5489	0.6177	0.8886	0.9191
	C_4H_9OH	0.5680	0.5899	0.9629	
	$C_6H_{13}OH$	0.5769	0.6374	0.905	
308.16	C_3H_7OH	0.6510	0.6790	0.9588	0.9532
	C_4H_9OH	0.6555	0.6941	0.9444	
	$C_6H_{13}OH$	0.6691	0.6996	0.9563	
318.16	C_3H_7OH	0.7045	0.7372	0.9557	0.9439
	C_4H_9OH	0.7081	0.7438	0.9521	
	$C_6H_{13}OH$	0.7309	0.7845	0.9317	

temperatures. The sixth column presents the $\nu_{C_6H_{14}}/\nu_{C_7H_{16}}$ ratios averaged over the alcohols for every value of temperature. No pattern is seen in the behavior of this parameter. The considerable spread of the values can be attributed to experimental inaccuracies in determining the concentrations since the compositions of all the mixtures are very close to the edges of the concentration interval.

Thus, the experimental material allows the tentative conclusion that the ratio $\nu_{C_6H_{14}}/\nu_{C_7H_{16}}$ does not depend on the intermediate component used in the calculation. Since the perfluorohexane–perfluoroheptane system is a highly soluble mixture without decomposition signs, there is no opportunity to obtain the ratio $\nu_{C_6H_{14}}/\nu_{C_7H_{16}}$ from the corresponding boundary curve. As well, the proposed procedure makes it possible to obtain information about a mixture in the absence of experimental data from which it could be derived directly. It should be remembered that ν is the characteristic frequency of a pure component and, therefore, can be expressed via macroscopic and microscopic properties of this component.

The practical value of the results is that, given two reliable anchor points, the critical concentration of decomposition can be determine even if the anchor

points are far from the critical point. In addition, formulas (1) and (2) make it possible to reconstruct one of the branches of the boundary curve from experimental data obtained for the other branch. The results confirm the feasibility of implicit determination of the frequency ratio ν_A/ν_B in the absence of direct experimental data for the boundary curve of $A-B$ system given the experimental data for $A-C$ and $B-C$ systems at the same temperature. This assertion proved valid for the case of mixtures consisting of fluorine-substituted hydrocarbons and alkanols and should be subject to verification with other systems.

The constancy of the ratio ν_A/ν_B obtained from different combinations provides an opportunity to analyze solubility in a liquid mixture on the basis of data for the pure components.

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