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Abstract

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Physicochemical Analysis of Binary Liquid Systems by Measurements of Boiling Temperatures

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The boiling temperature is one of the properties of the equilibrium liquid–vapor system. It can characterize the state of liquid systems in the same way that the melting temperature characterizes the state of solid phases. The successful application of thermal analysis of solid phases, as well as the results of investigations of the elasticity of vapor of solutions, testify to the applicability of boiling-temperature measurements also in physicochemical analysis ([1,2]).

At the present time, a large number of systems have been studied by boiling temperatures, the most detailed being systems without chemical interaction, containing an associated component ([3]). Irrational systems, whose number is approximately 300 ([13,10]), and normal systems have been studied in less detail. However, a considerable part of these investigations was carried out in searches for azeotropes, often without studying the boiling temperature of the system as a whole. Rational systems have not previously been investigated ebulliometrically, with the exception of one, $P_2O_5{-}H_2O$, which was also studied incompletely ([4]).

This experimental material, its classification, and theoretical interpretation in the literature are insufficient for substantiating the applicability of boiling-temperature measurement in physicochemical analysis. For this it is necessary to study the influence of chemical interaction between components on the boiling temperature of the systems formed by them. In other words, it is necessary to carry out an investigation of a series of typical rational and then irrational systems, first establishing the form of the boiling isobars of normal and associated systems.

It is known that the vapor pressure of a normal system is related to the molar composition by a linear dependence (Raoult’ s law). As a result, the curve of boiling temperatures of a normal system appears to us as slightly convex toward the composition axis. Curves of this type are also presented in the literature. However, when the boiling temperatures of the components are sufficiently close, a shallow minimum is possible on the isobar ([5]).

The boiling curve of associated systems, for which positive deviations from Raoult’ s law are observed, is convex toward the concentration axis of the diagram and lies below the normal boiling isobar.

In addition to the data of other authors, we have studied two such systems: dioxane—ethylene glycol and nitrobenzene—isobutyl alcohol. Their boiling isobars are of the same type and have a considerable negative deviation from the normal curve. This is associated with the dissociation of associated molecules of the components upon their dissolution.

Determination of the boiling temperature and of the composition of the vapor was carried out by us in an ebulliometer, which was a certain modification of the instruments of V. A. Kireev (^{6}) and Świętosławski (^{7}). The pressure in the instrument was kept constant by means of a manostat with electromagnetic regulation. The temperature was measured with calibrated mercury thermometers; the composition

the condensate was determined refractometrically and, in individual cases, by measurements of other physical properties of the condensate.

The boiling isobars of rational systems may have three types of singular points: upper, middle, and lower.

We investigated six rational systems, and two types of boiling isobars were obtained (with upper and middle singular points). The most characteristic isobars of the first type were obtained for the systems: piperidine—allyl mustard oil and ethylenediamine—allyl mustard oil.

Fig. 1 Fig. 2

Fig. 1 **Fig. 2**

The boiling curves of the first of these (Fig. 1) consist of two branches convex toward the composition axis, intersecting at the singular point corresponding to a component ratio of 1 : 1. The latter circumstance indicates the formation of the nondissociating compound $C_3H_5NHCSC_5H_{10}N$, also detected on the curves of other properties (1). On the vapor line the singular point corresponding to the compound is not sufficiently distinct. Such a course of the condensation curve, when its branches at first lie along the ordinates of the components and then, bending, meet at an obtuse angle, can be explained by the fact that the compound formed has a considerably greater heat of evaporation and boiling temperature than the components.

The boiling isobar of the system C_3H_5NCS—$C_2H_4(NH_2)_2$, essentially no different from that described above, has a singular point at the ordinate 66.7 mol.% C_3H_5NCS. This indicates the formation, in accordance with data from the study of other properties of the system (8), of the nondissociating compound $(C_3H_5NHCSNH)_2C_2H_4$.

The systems water—acetic anhydride and diphenylamine—maleic anhydride have a boiling isobar with a middle singular point at the ordinate 50 mol.%.

The condensation curve of the system water—acetic anhydride (Fig. 2) consists of two branches with different signs of curvature, intersecting, as does the evap-

Fig. 3

Figure 1: Fig. 3

Fig. 4

Figure 2: Fig. 4

oration curve, at a singular point indicating the existence in the vapors of a nondissociating compound (acetic acid).

A boiling isobar with a lower singular point could not be detected experimentally, and there are no mentions of them in the literature. However, using the method of models (9), one may conclude that this type of boiling isobar is geometrically admissible.

Along with singular points, azeotropes composed of the compound and one of the components are simultaneously possible on the isobars. This is observed

were observed in the systems we studied: diethylamine—phenyl mustard oil and ethylaniline—phenyl mustard oil. The formation of an azeotrope in the first of these systems with a minimum (Fig. 3), and in the second with a maximum boiling point, indicates the stability of the thiourea that forms and its existence on boiling as an individual compound. The ordinates of the singular points of the boiling isobars, as should be expected, do not shift with changes in pressure; the composition of the azeotrope, on the contrary, changes.

By smoothing the singular points of rational systems and smoothly transforming into one another the branches of the boiling isobars, we obtain the corresponding types of boiling isobars

Fig. 3

Fig. 4

of irrational systems. In irrational systems, the formation of compounds most often leads to the appearance of a minimum on the vapor-pressure isotherm or, correspondingly, a maximum on the boiling-temperature isobar (10).

The composition of the azeotropic mixture that arises as a consequence of compound formation in these systems may differ to a greater or lesser degree from the composition of the compound; the position of the maximum on the curve depends on the difference between the boiling points of the components.

When a comparatively stable and only slightly volatile compound is formed in systems with components whose boiling temperatures do not differ too greatly, the composition of the azeotropic mixture should be close to the composition of this compound, and in some systems it even coincides with it (3). In these cases it may be asserted that the maximum azeotrope is a chemical compound. This conclusion is especially convincing when the composition of the azeotrope does not shift with changes in pressure and coincides with the composition of the extrema of isotherms of other properties, which testify to the formation of a compound in the system.

Examples of such systems are H_2O—SO_3 (11), $C_6H_5NH_2$—HCl (12), CH_3COOH —$(C_2H_5)_3$ (13), systems with BF_3 (3), and others.

We have carried out an ebulliometric study of five irrational systems. The boiling isobars of the system stannic chloride—ethyl acetate (for 52 and 100 mm Hg) are continuous curves with maxima at 35.0 and 36.0 mol.%, respectively.

These data reflect, in our opinion, the interaction in the system leading to the formation of the compound: $SnCl_4 \cdot 2HC_2COOC_3H_5$, and are consistent with the results of studying other physical properties.

Close to the system considered is the system PCl_3—C_6H_5CHO. The boiling curves for five different pressures consist of two parts convex toward the composition axis, passing into one another at a clearly expressed maximum at ordinates from 76.0 mole % at 152 mm to 79.0 mole % C_6H_5CHO at 360 mm Hg. The maximum of the boiling isobars is close to the composition of the extrema of the isotherms of properties obtained earlier ([14]) and characterizes the formation in the system of a compound of composition $PCl_3 \cdot 3C_6H_5CHO$.

The systems chloral—water and chloral—ethyl alcohol have previously been investigated in part by boiling temperatures. The boiling isobar of the first of them at 740 mm ([15]) (Fig. 4) has no characteristic features indicating the formation of a compound in the system. However, the boiling isobars obtained by us at lower pressures are smooth curves with a maximum approaching the ordinate 50 mole % CCl_3CHO, characterizing the formation of the compound $CCl_3CHO \cdot H_2O$ (in the second system, $CCl_3CHO \cdot C_2H_5OH$). There are data that the indicated compounds exist in the vapor phase ([16]).

The boiling isobars of the ethylenediamine—water system (at five different pressure values) are smooth lines with a flat maximum at 50 mole %. The maximum azeotrope corresponds to the monohydrate of ethylenediamine that is formed.

As a result of the investigation carried out, it has been shown that the measurement of boiling temperature and vapor composition agrees with data from the study of other physical properties and substantially supplements them. They make it possible to establish the presence of interaction in the liquid and vapor phases of the system and to characterize the stability of the compounds formed under boiling conditions.

All this leads us to the conclusion that ebullioscopic measurements can serve as an effective method of physicochemical analysis of liquid systems.

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Note: Figure translations are in progress. See original paper for figures.