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Abstract

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On the Nature of S-Shaped Viscosity Diagrams of Binary Systems

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The classification of viscosity isotherms of liquid systems ([1]) combines four principal types of diagrams. Type I consists of isotherms convex toward the composition axis (a special case is curves with a minimum). According to the generally accepted interpretation of such diagrams, isotherms of this kind do not reflect interaction between the components. Type II consists of isotherms with a viscosity maximum (this type also includes the comparatively rare isotherms convex away from the composition axis but having no extrema). Type III consists of viscosity diagrams with a singular point. Finally, type IV consists of diagrams with S-shaped isotherms.

Viscosity diagrams with S-shaped isotherms occupy a special place in comparison with the other types of isotherms. Whereas the first three types make it possible to draw a qualitative conclusion about the degree of chemical interaction (which increases from type I to III), the interpretation of S-shaped isotherms is always limited merely to establishing the fact of chemical interaction between the components of the system.

The first analysis of S-shaped viscosity isotherms was carried out by M. I. Usanovich ([2,3]), who showed that, when the temperature is lowered, S-shaped isotherms do not tend to pass into curves with a maximum. In a number of cases S-shaped isotherms were realized even when the system was studied in the supercooled state—below the crystallization temperature of the compound formed. According to M. I. Usanovich' s interpretation, S-shaped viscosity isotherms are realized when the viscosity of the compound formed has an intermediate value between the viscosities of the initial components.

A determination of the relationship between S-shaped viscosity diagrams and diagrams of the other three types can be obtained by comparing the viscosity of a series of binary systems in which one and the same component (A) reacts with other components (B, C), whose activity with respect to it has been established by independent methods. Several such series are given below, in which one of the diagrams is S-shaped.

In the series acetic acid—acids (Table 1), the degree of chemical interaction decreases from the system with perchloric acid to the system with propionic

acid. As the investigations of M. I. Usanovich and co-workers ([4,5]) have shown, acetic acid in all these systems, with the exception of the last, exhibits a basic function.

With respect to perchloric acid, the majority of acids, with the exception of sulfuric and trichloroacetic acids, exhibit a clearly expressed basic function ([11–13]). Therefore, in the series perchloric acid–acids (Table 1), the degree of chemical interaction increases from the system with sulfuric acid to the system with water.

In accordance with the degree of chemical interaction in these two series, the relative viscosity maximum changes (the ratio of the viscosity maximum ···

Table 1

Second component	Intrinsic viscosity of the second component, cP	Magnitude of the viscosity maximum	Relative viscosity maximum	Source
Viscosity of systems of the series acetic acid–acids at 25°	**Viscosity of systems of the series acetic acid–acids at 25°**	**Viscosity of systems of the series acetic acid–acids at 25°**	**Viscosity of systems of the series acetic acid–acids at 25°**	**Viscosity of systems of the series acetic acid–acids at 25°**
$HClO_4$	0.795*	42.0	52.8	(4)
H_2SO_4	23.17	110.16	4.75	(6)
HNO_3	0.82	1.874	2.29	(7)
H_3PO_4	164.7	244.8	1.49	(8)
$CH_2ClCOOH$	S-shaped isotherm	S-shaped isotherm	S-shaped isotherm	(9)
C_2H_5COOH	Isotherm convex toward the composition axis	Isotherm convex toward the composition axis	Isotherm convex toward the composition axis	(10)

Second component	Intrinsic viscosity of the second component, cP	Magnitude of the viscosity maximum	Relative viscosity maximum	Source
Viscosity of systems of the series hydrochloric acid–acids at 50°	**Viscosity of systems of the series hydrochloric acid–acids at 50°**	**Viscosity of systems of the series hydrochloric acid–acids at 50°**	**Viscosity of systems of the series hydrochloric acid–acids at 50°**	**Viscosity of systems of the series hydrochloric acid–acids at 50°**
H_2SO_4	Isotherm convex toward the composition axis	Isotherm convex toward the composition axis	Isotherm convex toward the composition axis	(11)
CCl_3COOH	The same	The same	The same	(12)
$CHCl_2COOH$	S-shaped isotherm	S-shaped isotherm	S-shaped isotherm	(13)
$CH_2ClCOOH$	2.15**	3.55	1.65	(15)
CH_3COOH	0.742	12.68	17.1	(4)
H_2O	0.549	31.91	58.2	(16)
Viscosity of systems of the series monochloroacetic acid–acids at 60°	**Viscosity of systems of the series monochloroacetic acid–acids at 60°**	**Viscosity of systems of the series monochloroacetic acid–acids at 60°**	**Viscosity of systems of the series monochloroacetic acid–acids at 60°**	**Viscosity of systems of the series monochloroacetic acid–acids at 60°**
$HClO_4$	0.55	2.44	4.0	(15)
H_2SO_4	9.30	10.2	1.1	(17)
HNO_3	Isotherm convex toward the composition axis	Isotherm convex toward the composition axis	Isotherm convex toward the composition axis	(17)
CH_3COOH	S-shaped isotherm	S-shaped isotherm	S-shaped isotherm	(9)
C_6H_5OH	2.521	2.527	1.0	(18)

* According to data of (5).
** According to data of (14).

···to the magnitude of the viscosity of the second component of each system of the corresponding series). The relative viscosity maximum, which takes into account the influence on the magnitude of the maximum of the intrinsic viscosity of the second component of each system of the corresponding series, is introduced in the present case as a quantity that well illustrates the qualitative change in the degree of chemical interaction in a binary system (19).

From the data in Table 1 it is seen that systems with S-shaped isotherms are transitional from systems with a well-expressed interaction to systems in which the viscosity isotherms do not reflect interaction between the components. An analogous picture is observed in the series chloroacetic acid—acids. With respect to strong acids—hydrochloric and sulfuric—chloroacetic acid plays the role of a base, which leads to an interaction reflected in the viscosity diagrams. With a weaker acid—nitric—chloroacetic acid either no longer interacts, or interacts to such an insignificant degree that this is not reflected in the viscosity diagrams. In systems with acetic acid and phenol, a reversal of functions occurs: chloroacetic acid exhibits its acidic properties. Correspondingly, the degree of chemical interaction increases as the acidic properties of the second components weaken, i.e., from acetic acid to phenol.

In this case as well, S-shaped viscosity diagrams appear as an intermediate stage between systems with a well-expressed chemical interaction and systems in which interaction either does not occur at all or is manifested to a very insignificant degree.

The intermediate position of diagrams with S-shaped isotherms is also clearly illustrated by other series analogous to those presented above.

(nicotine—chlorinated hydrocarbon derivatives, esters—acetic acid, etc.).

The extensive experimental material accumulated to date on viscosity diagrams of binary liquid systems leaves no doubt that chemical interaction proceeding according to the scheme $A + B = AB$ is always associated with an increase in viscosity. In light of this, it should be considered that S-shaped viscosity diagrams occur in those cases where the viscosities of the initial components differ appreciably from one another, and the amount of the compound formed is insufficient to exceed the viscosity of the more viscous component.

Thus, a genetic connection is manifested between diagrams with isotherms convex toward the composition axis and diagrams with a viscosity maximum—a connection in which S-shaped isotherms are an intermediate link.

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