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REFRACTOMETRY AS A METHOD FOR THE PHYSICOCHEMICAL ANALYSIS OF ORGANIC SYSTEMS

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INTRODUCTION

Refractometry was the first optical method to be applied in chemistry and it has been widely used for structure determination, identification, and quantitative analysis. Less attention has been paid to the possibility of using refractometry for physicochemical analysis, i.e. to gain information about the interaction between the components of chemical systems and on their association or dissociation, from the shape of the refractive index vs. composition curves.

The organic chemist faced with the necessity of studying the nature of liquid systems in connection with problems of molecular-compound formation and the mechanism of organic reactions finds the universal, readily available, and simple refractometric method extremely attractive. The present article describes critically the basis of the refractometric method of physicochemical analysis and the history of its application to organic systems, and examines the possibility of further applications. A critical analysis is also of interest in connection with the study of the methodology of physicochemical analysis as developed by N. S. Kurnakov (1860–1941) and his school. In the works of Anosov, Pushin, and Trifonov, we find the statement and interpretation of the relationships between the shapes of property vs. composition diagrams and the physicochemical processes in the systems studied, in terms typical of Kurnakov's methodology. The study of this methodology extends beyond the refractometric method, and is of interest in relation to the critical evaluation of analogous methods based on the measurement of other properties, such as dielectric constant, surface tension, viscosity, etc.

In the present paper we shall restrict ourselves to binary systems, but the principal features established for binary systems also hold for ternary systems.

I. ORIGINS OF THE REFRACTOMETRIC METHOD OF PHYSICOCHEMICAL ANALYSIS AND ITS DEVELOPMENT IN THE FIRST HALF OF THE 20TH CENTURY

The possibility of using refractometry for the study of compounds formed in solution appears to have been first indicated in a paper by Deville[1], who detected refractive-index maxima in aqueous solutions of acetic acid and methyl and ethyl alcohols. Deville noted that the position of the maxima corresponded closely to integral molar ratios of the components, and expressed the hope that the singular points on the refractive-index curves might be used to study compounds in solution. This idea, however, was not developed until 50 years later.

Fery[2] found that the equivalence points in neutralisation reactions corresponded to angular points on the refractive-

-index isotherms of the mixed solutions. In such systems, according to Fery, the refractive-index curves consist of intersecting straight lines.

Almost simultaneously, the effect of double-decomposition reactions in salt solutions on the values of the refractive index was examined by Verschaffelt[3], who studied mixtures of solutions having almost identical refractive indices. With this choice of concentrations of the solutions to be mixed, deviations from additivity led to the appearance of maximum and minimum refractive-index values. From a survey of the conditions under which these values were obtained, Verschaffelt concluded that in mixed electrolyte solutions, negative deviations from additivity characterised chemical interaction between the components, while positive deviations indicated chemical interaction only when they could not be attributed to contraction, since maximum values of n were observed when very concentrated solutions of salts with identical refractive index were mixed, even when no reaction took place between the dissolved salts.

Verschaffelt also detected refractive-index maxima in mixtures of water with butyric and valeric acids, and noted that the maxima were displaced to higher concentrations of acid with increase in the molecular weight of the latter[4]. Refractive-index maxima were also observed in mixtures of carboxylic acids and alcohols (of similar structure), but these did not correspond to equimolar compositions. One of the first successful attempts to use refractometry to detect unstable organic compounds was made in an investigation of the acetaldehyde–ethyl alcohol system[5]. A clearly defined maximum value of n_D^{18} was observed at an equimolar component ratio, indicating hemiacetal formation.

In addition to the study of refractive-index curves, attempts were made at the start of the 20th century to find the relationship between the deviations of molecular refractions from additivity and the non-ideal nature of binary systems, particularly as revealed by deviations from Raoult's law. In azeotropic systems, however, additivity of molecular refraction was observed, except in a few cases[6]. Similarly, no direct relationship could be found between the sign of the deviation from additivity of the molecular refractions and vapour pressures[7].

At the end of the 19th and start of the 20th centuries, an attempt was made to use refractometry to confirm Mendeleev's hydrate theory of solutions and to establish the effect of electrolyte dissociation on the refractive properties (by Pickering, Jones, Leblanc, Walden, and others), but a discussion of this work is beyond the scope of the present article. In a review of the above early works on the refractometric study of solutions, Kremann[8] pointed out that deviations of the refractive properties from additivity are possible, but not essential, features of association and dissociation processes. On the other hand, deviations from a linear relationship are observed even in the absence of interaction, so that the study of the refraction of light, in Kremann's opinion was "little suited to the examination of the constitution of binary liquid mixtures".

The subsequent development of the refractometric method of physicochemical analysis was closely related to the work of Kurnakov and his school. From 1908–1909 onwards, they undertook an extensive study of organic systems by the various methods of physicochemical analysis, and Glazunov, a graduate of the Polytechnic Institute, undertook the study of the refractive index vs. composition diagrams[9].

Glazunov studied 9 binary organic systems, classifying them into three groups according to the nature of the interaction between the components:

Group 1. The refractive index is a linear function of the composition (in mole fractions) — systems where no chemical interaction takes place (benzene–aniline, chloroform–bromoform, etc.).

Group 2. The refractive-index diagram consists of two straight lines intersecting at a point corresponding to a non-dissociated compound — "rational" systems (Kurnakov's terminology) such as mustard oils–secondary amines.

Group 3. Curves are obtained (sometimes with a maximum) — "irrational" systems in which unstable dissociated compounds are formed (acetone–water, acetic acid–aniline, etc.).

Glazunov's classification of refractive index diagrams was based on a limited number of not very accurate data. The problem of the relationship between the shape of the refractive-index curves and the nature of binary systems was examined much more thoroughly by Anosov[10–12]. Like Glazunov, he considered it necessary to construct the refractive-index diagrams using mole percentages to express the composition. From a study of 15 systems and the literature data for approximately 50 more, Anosov modified Glazunov's classification as follows:

1) The branches of the diagrams with singular points should in general be curves, and not straight lines.

2) The isotherms of the third group are characterised not by general curves, but by curves convex away from the concentration axis.

3) A further group of isotherms must be introduced — — those convex towards the axis of abscissae and characteristic of systems with a component which dissociates on dissolution in the other.

Thus according to Anosov there existed four classes of refractive-index isotherm, each of which reflected a definite type of interaction between the components in binary systems.

1) Straight lines, or lines with very small curvature, usually convex towards the composition axis — ideal or almost ideal (normal) systems.

2) Curves with a marked convexity towards the composition axis — systems in which one component dissociates on dissolution in the other.

3) Curves with a marked convexity away from the composition axis (sometimes with a maximum) — "irrational" systems, where a more or less extensively dissociated compound is formed.

4) Curves with a singular point, consisting of two intersecting branches and observed only in rational systems where an undissociated compound is formed.

Anosov's classification was completely analogous to that of other composition vs. property diagrams, developed by Kurnakov's school, and appeared in basic text-books on physicochemical analysis[13,14].

The principles upon which Anosov based his interpretation of the shape of the non-singular refractive-index isotherms may be formulated as follows:

1) In ideal systems the refractive index is an additive function of the mole fractions of the components:

$$n = n_1 N_1 + n_2 N_2 \qquad (1.1)$$

where n_1 and n_2 are the refractive indices of the components

and N_1 and N_2 are their mole fractions.

2) The nature of the chemical processes taking place in the system determines uniquely whether the $n(N)$ isotherms are convex or concave towards the x-axis*. The formation of compounds leads to *positive* deviations from additivity $\Delta n(N)$:

$$\Delta n(N) = n_{exp} - n_1N_1 - n_2N_2, \quad (1.2)$$

and dissociation of associated components leads to the opposite effect — *negative* deviations $\Delta n(N)$.

During the nineteen-thirties and -forties, the great majority of papers on the application of refractometry to the study of organic systems was based on these principles and on the corresponding classification of refractive-index curves. Particular mention must be made of the extensive studies carried out by the noted Russian chemist Pushin and his school at Belgrade University[15-45]. The refractometric method was also used for the study of organic systems by Trifonov and his school[46-55] and others[56-66].

The above principles are apparently completely logical. However, attempts to apply the classification in practice have led to numerous difficulties and contradictions.

By attributing significance even to small deviations from additivity $\Delta n(N)$ of the order of $1-2\times10^{-3}$, Anosov concluded that the positive values of $\Delta n(N)$ in the dimethylaniline–allyl isothiocyanate system indicated "some chemical interaction"[10,12]. This conclusion contradicts the well-known fact that tertiary amines do not react with isothiocyanates, and is not in accordance with viscosimetric data. Anosov tried to explain these and certain other analogous cases of non-correspondence between the refractive-index curves and other properties by postulating, for almost all substances, a certain tendency to undergo chemical interaction and also to undergo association[12-14]. "If one of these tendencies is marked, then it appears on the isotherms for all the properties, and suppresses the other. For systems close to ideal, however, neither tendency predominates, although it is possible that the isotherms for different properties have different sensitivity towards these tendencies...."[12].

This interpretation, although it may be applicable to normal systems, is not applicable to those showing considerable deviations from ideal behaviour. At the same time, non-correspondence between refractometric and other properties has for long been known even in typical irrational systems.

Ust'-Kachkintsev[65] studied the ethylene diamine–water system and pointed out that refractometry indicates only the existence of the dihydrate $C_2H_4(NH_2)_2 \cdot 2H_2O$. The formation of the stable monohydrate, whose existence in the liquid phase is undisputed, cannot be detected.

A number of very strange cases of non-correspondence between the shape of the refractive-index curves and the diagrams typical of irrational systems was observed by Matavul'[30,32]. In mixtures of quinoline and pyridine with higher fatty acids — oenanthic, caprylic, pelargonic and capric — *negative* deviations from additivity $\Delta n(N)$ were observed and the $n(N)$ curves had the shape typical of systems with non-interacting associated components, although in these systems acid-base interaction undoubtedly takes place. At the same time, mixtures of lower carboxylic acids with the same bases showed positive deviations $\Delta n(N)$ (Fig. 1). This curious change in the sign of the $n(N)$ isotherms on going from the lower members of the homologous series to the higher could not then be satisfactorily explained*. Despite the convictions of Anosov[13,14], who did not know of this work, the existence of negative $n(N)$ isotherms in irrational systems showed that class 2 of his classification was not distinct.

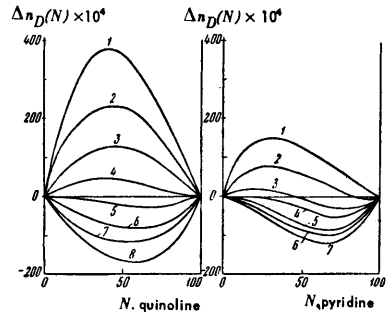


Fig. 1. Deviations of the refractive index from additivity, $\Delta n(N)$, in mixtures of quinoline and pyridine with carboxylic acids: 1) propionic; 2) butyric; 3) valeric; 4) caproic; 5) oenanthic; 6) caprylic; 7) pelargonic; 8) capric.

In connection with the difficulties encountered in the refractometric study of irrational systems, mention must be made of the work of Usanovich and Stepan'yants[66]. In the arsenic trichloride–diethyl ether system, where electrical conductivity and viscosity data show that a compound of equimolecular composition is formed, these authors found an almost linear $n(N)$ isotherm, which, according to Glazunov, Anosov, and Pushin, was characteristic of ideal systems. This contradiction led Usanovich and Stepan'yants to doubt the accuracy of formula (1.1) for refractive-index additivity. Referring to an early paper by Pulfrich[67] on the relationship between refractive index and the density of solutions, they pointed out that in ideal systems the refractive indices should be additive as functions of the component concentrations expressed in *volume* fractions:

$$n = n_1V_1 + n_2V_2. \quad (1.3)$$

When this is done, positive deviations from additivity are obtained in the $AsCl_3$–$(C_2H_5)_2O$ system

$$\Delta n(V) = n_{exp} - n_1V_1 - n_2V_2, \quad (1.4)$$

and the disagreement with data obtained by other methods disappears.

* The symbol $n(N)$ denotes the refractive index n, regarded as a function of the composition expressed as the mole fraction N. The functional dependence of n on composition in volume V and weight P fractions will be denoted by $n(V)$ and $n(P)$ respectively.

* Matavul' tried (on insufficient factual grounds) to ascribe it to "the influence of association of the acids"[30, 30,32].

In work on the refractometric method of physicochemical analysis, uncertainty in the formulation of the additivity rule existed long before 1940 and has continued until very recent times. The formulation (1.3) was used by Verschaffelt[3], and the necessity of using this form was confirmed by Mac-Farlane and Wright[68], but their views were completely ignored in work on physicochemical analysis. Until 1947, Trifonov and his school used rule (1.1) exclusively[46-48], but since then they have considered the $n(V)$ curves *together with* the $n(N)$ curves[49-52], with the statement that in a number of cases the former are more demonstrative[51]. Trifonov and his school, however, have not attributed fundamental significance to this formulation of the additivity rule, and have occasionally used mole fractions alone[53-55]. Certain workers[69], moreover, have constructed refractive-index diagrams with composition expressed in *weight* fractions (or percentages), formulating the additivity rule in the form

$$n = n_1P_1 + n_2P_2, \tag{1.5}$$

and regarding the deviations from additivity as

$$\Delta n(P) = n_{exp} - n_1P_1 - n_2P_2. \tag{1.6}$$

From the point of view of scientific logic, it is curious that Pushin, who in his first works[15,16] considered $\Delta n(N)$, in his third paper[17] changed, without comment, to the construction of the $n(P)$ diagrams and the interpretation of the deviations from additivity $\Delta n(P)$. In the many subsequent papers from the Belgrade school[18,20-28,30-40], the $n(N)$ diagrams were again used, and only occasionally the quantities $n(P)$, together with $n(N)$.[19,29] Without being able to explain the non-correspondence between the shape of the $n(N)$ curves and the chemical character of the systems studied, Pushin in such cases simply changed the abscissae of the refractive-index diagrams in such a way as to give the curve the desired shape, agreeing with other data on the behaviour of the components.

Analogous difficulties were encountered by English workers[56]: in the typical eutectic system acetic acid—chlorobenzene, very *pronounced positive* deviations from additivity $\Delta n(N)$ were observed, which were several times greater than the values of $\Delta n(N)$ for the irrational *p*-toluidine–*o*-chlorophenol and *p*-toluidine–*p*-chlorophenol systems.

In 1939 Trifonov and Aleksandrov[46] made an extensive examination of their own and literature data and showed that positive deviations $\Delta n(N)$ were extremely common in systems formed by non-interacting associated components. They pointed out the existence of more than 40 systems of this type, with $n(N)$ curves concave towards the composition axis, instead of convex, as required by Anosov's classification. Anosov[13,14] admitted the indefinite character of the 3rd group of his classification and the impossibility of distinguishing systems formed by non-interacting associated components with positive $\Delta n(N)$ from typical irrational systems, from the shape of the $n(N)$ isotherms. It was still not clear which systems with associated components gave positive values of $\Delta n(N)$ and which gave negative deviations. Trifonov and Aleksandrov[46] postulated the existence of two types of association by molecules of the components. Others[63,70] tried to relate a positive sign for $\Delta n(N)$ to contraction on mixing the components, but it will be seen in Section III that this interpretation is incorrect.

The history of the application of refractometry to the study of the behaviour of components in organic systems reveals a great deal of inexplicable contradictions, which must be regarded as a result of the purely empirical approach to the problem and neglect of the theory of specific and molecular refractions. Study of the works cited shows that it is necessary to re-examine the fundamental postulates of the refractometric method of physicochemical analysis and to put it on a more rigorous basis. The subsequent sections give the results of investigations with this objective, carried out since 1951.[71-79]

II. THE ADDITIVITY OF REFRACTIVE INDICES

The above review of the literature shows that conclusions about the nature of the interaction between the components of organic systems from the shape of the refractive-index curves were most frequently based on the direction of the convexity of the curves, i.e. on the *sign of the deviations from additivity*. In the great majority of papers[9-16,18-28,30-40,46-65] and text books[13,14], the additivity of $n(N)$ (1.1) was assumed, the additivity of $n(V)$ (1.3) and $n(P)$ (1.5) being assumed only in a few cases. In all these papers, no great significance was attached to the foundations of the additivity rule, and no particular attention was paid to it, although the formulation of the rule is of fundamental importance to any conclusions based on deviations from additivity.

Let us examine this problem from the point of view of specific-refraction theory. Many formulae have been proposed for the specific refraction r, and these may all be written in the general form

$$r = \frac{f(n)}{d}, \tag{2.1}$$

where d is the density of the substance and $f(n)$ is a function of the refractive index, the form of which depends on the particular physical theories of optical refraction and on the magnitude of the internal electric field in the dielectric, acting on a molecule surrounded by polarised molecules.

Examples of the more familiar functions $f(n)$ are:

$$f(n) = n - 1 \quad \text{(Gladstone–Dale)}, \tag{2.2}$$

$$f(n) = n^2 - 1 \quad \text{(Newton–Laplace)}, \tag{2.3}$$

$$f(n) = \frac{n^2-1}{n^2+2} \quad \text{(Lorentz and Lorenz)}, \tag{2.4}$$

$$f(n) = \frac{(n^2-1)[2n^2+1+2\alpha(n^2-1)/a^3]}{n^2}, \tag{2.5}$$

where α is the polarisability of the molecule and a its radius (Böttcher's formula).

The last of these formulae contains the characteristic molecular parameters α and a, which indicates that there is no absolute rigorous, universal expression for the specific refraction, independent of the nature of the substance in question.

The rule for specific-refraction additivity in binary systems in its general form, may be written

$$r = r_1P_1 + r_2P_2 \tag{2.6}$$

or

$$\frac{f(n)}{d} = \frac{f(n_1)}{d_1}P_1 + \frac{f(n_2)}{d_2}P_2 \tag{2.7}$$

From this it follows that

$$f(n) = f(n_1)V_1 + f(n_2)V_2, \tag{2.8}$$

where $V_1 = \frac{dP_1}{d_1}$ and $V_2 = \frac{dP_2}{d_2}$ are the volume fractions of the components of the mixture. Thus this function should be

additive when the *volume* fractions are used, *irrespective* of the choice of function $f(n)$.

According to modern views [80], universal functions $f(n)$ can correspond only approximately to the additivity condition (2.8), even though the degree of accuracy is very high. According to experimental data obtained towards the end of last century and still valid today [81,82], the Gladstone–Dale formula (2.2) corresponds to the additivity condition (2.8) better than formulae (2.3) and (2.4). Thus when $f(n) = n-1$ and $V_1 + V_2 = 1$ (ideal systems with no volume change), the additivity rule (2.8) becomes

$$n = n_1V_1 + n_2V_2 . \qquad (2.9)$$

Thus the refractive indices of ideal systems are additive functions of volume fractions. Although the Gladstone–Dale formula reproduces experimental data for liquid systems slightly better than the other refraction formulae, it is still not completely rigorous and universal, and the statement that $n(V)$ is additive in ideal systems cannot be regarded as completely rigorous. This feature must be taken into account, although it becomes important only for the interpretation of fairly small deviations from additivity $\Delta n(V)$.

The additivity rules (1.1) and (1.5), which figure in the great majority of papers on refractivity in organic systems, are thus seen to contradict specific-refraction theory. The question then arises of whether this contradiction is real in practice as well as in principle.

There is an absolutely rigorous and universal relationship between the deviations from additivity $\Delta n(N)$, $\Delta n(V)$, and $\Delta n(P)$, (1.2), (1.4), and (1.6)

$$\Delta n(N) = \Delta n(V) + (n_1 - n_2)(V_1 - N_1) , \qquad (2.10)$$

and

$$\Delta n(P) = \Delta n(V) + (n_1 - n_2)(V_1 - P_1)^* , \qquad (2.11)$$

so that the relationship between the various formulations of the deviations from additivity is determined by the magnitude of the terms $(n_1-n_2)(V_1-N_1)$ and $(n_1-n_2)(V_1-P_1)$ on the one hand, and the magnitude of $\Delta n(V)$ on the other. The differences between the formulations of the additivity rules (1.1), (1.3), and (1.5) may be neglected when

$$|(n_1 - n_2)(V_1 - N_1)| \ll |\Delta n(V)| , \qquad (2.12)$$

or

$$|(n_1 - n_2)(V_1 - P_1)| \ll |\Delta n(V)| . \qquad (2.13)$$

As a rule, these conditions are not fulfilled. The deviations from additivity $\Delta n(V)$ are usually of the order of 10^{-2}–10^{-3}, and the differences n_1-n_2 are of the order of 10^{-1}–10^{-2}. The discrepancy between the different forms of expressing the concentration depends on the relationship between the properties of the components and often amounts to 10^{-1}, so that the terms $(n_1-n_2)(V_1-N_1)$ and $(n_1-n_2)(V_1-P_1)$ are usually of the same order of magnitude as $\Delta n(V)$.

The magnitude and sign of the deviations from additivity $\Delta n(N)$ and $\Delta n(P)$ depend not only on the behaviour of the components of the mixtures, but also to an equal extent on the relationship between their properties (molar volumes and densities). In real cases

$$|(n_1 - n_2)(V_1 - N_1)| > |\Delta n(V)| , \qquad (2.14)$$

and

$$|(n_1 - n_2)(V_1 - P_1)| > |\Delta n(V)| , \qquad (2.15)$$

and the sign of the deviations from additivity $\Delta n(N)$ and $\Delta n(P)$ is determined entirely by the signs of the differences V_1-N_1 and V_1-P_1, i.e. the signs of these deviations will in such cases depend only on the relationship between the densities and molar volumes of the components:

when $d_2 > d_1$, $V_1 - P_1 > 0$ and $\Delta n(P) > 0$, (2.16)

and when $d_2 < d_1$, $V_1 - P_1 < 0$ and $\Delta n(P) < 0$, (2.17)

when $\frac{M_2}{d_2} < \frac{M_1}{d_1}$, $V_1 - N_1 > 0$ and $\Delta n(N) > 0$, (2.18)

and when $\frac{M_2}{d_2} > \frac{M_1}{d_1}$, $V_1 - N_1 < 0$ and $\Delta n(N) < 0$. (2.19)

From this it follows that the deviations from additivity $\Delta n(N)$ and $\Delta n(P)$ do not in general give direct information about the behaviour of the components of solutions. One of the chief reasons for the many misconceptions and contradictions noted in the previous section is the erroneous formulation of the refractive-index additivity rule (1.1). This may be illustrated by specific examples.

The change in sign of the $n(N)$ curves in pyridine and quinoline systems [30,32] on going from lower to higher carboxylic acids (Fig. 1) is simply explained. It is not related to association of the acids but results merely from the change in the relationship between the molar volumes of pyridine and quinoline (first components) and those of the acids (second components). Fig. 2 shows the calculated $\Delta n(V)$ curves for these systems. In all cases the positive deviation from additivity $\Delta n(V)$ characteristic of irrational systems is observed.

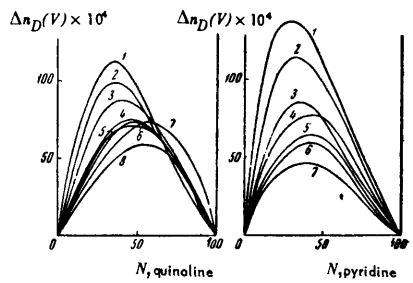


Fig. 2. Deviations from additivity, $\Delta n(V)$ in the same systems as those in Fig. 1.

In the mixtures with the simplest acids, $\frac{M_2}{d_2} < \frac{M_1}{d_1}$, i.e. relationship (2.18) holds, and the positive terms $(n_1-n_2)(V_1-N_1)$, added to the positive quantities $\Delta n(V)$, give extremely high values of $\Delta n(N)$. For the higher acids, $\frac{M_2}{d_2} > \frac{M_1}{d_1}$, and the negative terms at first reduce the positive values of $\Delta n(V)$, leading to the appearance of points of

* Eqns. (2.10) and (2.11) are particular cases of the general algebraic formula for the deviations from additivity of any property Z, regarded as a function of concentrations expressed in the different forms X and Y:

$$\Delta Z(Y) = \Delta Z(X) + (Z_1 - Z_2)(X_1 - Y_1).$$

inflection and afterwards to a change to negative $n(N)$ curves. The change in sign of the $\Delta n(N)$ curves in the pyridine systems takes place earlier than in the quinoline systems, since the molar volume of pyridine is less than that of quinoline.

The marked positive deviations from additivity $\Delta n(N)$ observed in many systems containing non-interacting associated components[46,56] are explained equally simply. These are usually obtained when $\frac{M_2}{d_2} < \frac{M_1}{d_1}$, and this is not related to the nature of the association of the components, as Trifonov and Aleksandrov suggested[46].

The erroneous formulation of the additivity rule (1.1) also explains the misconceptions of Aleksandrov[47] and others regarding the existence of stable molecular complexes in associated components. We have discussed this in detail elsewhere[78].

In the derivation of the additivity rule (2.9), we started from the additivity of specific refractions (2.6). The question arises of whether it is possible to base the choice of additivity rule on direct experiment, independently of the theory of specific or molecular refractions. When claiming linearity for the $n(N)$ isotherms of ideal systems, Anosov[10,12,14] and others referred to the results of the study of certain systems such as mixtures of "iso-fluid" liquids[83]. These systems usually consisted of isomers with very close refractive indices and almost identical molecular volumes (e.g. ethylbenzene and xylenes), so that the terms (n_1-n_2) (V_1-N_1) were very small and the $n(N)$ and $n(V)$ additivity rules (1.1) and (1.3) practically coincided. Experimental data on this type of system naturally cannot be used as argument for the choice of an additivity rule.

In order to make a justifiable choice between the rules (1.1), (1.3), and (1.5) directly based on experimental refractive-index data, it is necessary to examine normal systems made up of components satisfying the conditions

$$n_1 \gg n_2 , \tag{2.20}$$

$$M_1 \gg M_2 \quad \text{or} \quad M_1 \ll M_2 , \tag{2.21}$$

$$d_1 \gg d_2 \quad \text{or} \quad d_1 \ll d_2 , \tag{2.22}$$

$$\frac{M_1}{d_1} \gg \frac{M_2}{d_2} \quad \text{or} \quad \frac{M_1}{d_1} \ll \frac{M_2}{d_2} . \tag{2.23}$$

In addition, in order to avoid erroneous conclusions resulting from an arbitrary choice of systems, it is necessary to examine systems showing all six possible relationships between the properties of the components:

$$\text{I. } P_1 > V_1 > N_1 \left(\text{for } M_1 > M_2,\ d_1 > d_2 \text{ and } \frac{M_1}{d_1} > \frac{M_2}{d_2}\right), \tag{2.24}$$

$$\text{II. } P_1 > N_1 > V_1 \left(\text{for } M_1 > M_2,\ d_1 > d_2 \text{ and } \frac{M_1}{d_1} < \frac{M_2}{d_2}\right), \tag{2.25}$$

$$\text{III. } V_1 > P_1 > N_1 \ (\text{for } M_1 > M_2 \text{ and } d_1 < d_2) \tag{2.26}$$

$$\text{IV. } N_1 > P_1 > V_1 \ (\text{for } M_1 < M_2 \text{ and } d_1 > d_2) \tag{2.27}$$

$$\text{V. } V_1 > P_1 > P_1 \left(\text{for } M_1 < M_2,\ d_1 < d_2 \text{ and } \frac{M_1}{d_1} > \frac{M_2}{d_2}\right), \tag{2.28}$$

$$\text{VI. } N_1 > V_1 > P_1 \left(\text{for } M_1 < M_2,\ d_1 < d_2 \text{ and } \frac{M_1}{d_1} < \frac{M_2}{d_2}\right). \tag{2.29}$$

The results of our studies for all six types[71] are given in Fig. 3, which shows that the additivity rules (1.1) and (1.5) used earlier are incorrect.

In normal systems, the deviations from additivity $\Delta n(N)$ and $\Delta n(P)$ may be very large (0.02–0.03) and it is extremely significant that the magnitude and sign of these deviations have a distinct dependence on the relationships (2.24–2.29) and are therefore determined by the relationship between the molar volumes and densities of the components, and not

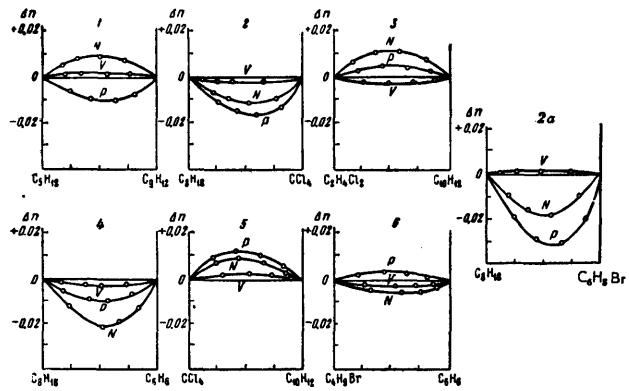


Fig. 3. Deviations of the refractive index from additivity with the composition expressed in mole, N, weight, P, and volume, V fractions in normal systems corresponding to conditions (2.20–2.23): 1) mesitylene–n-pentane; 2) carbon tetrachloride–2,2,4-trimethylpentane; 3) tetralin–dichloroethane; 4) benzene–2,2,4-trimethylpentane; 5) tetralin–carbon tetrachloride; 6) benzene–n-butyl bromide. The numbering of the systems corresponds to relationships I–VI (2.24–2.29).

by their behaviour in mixtures. The values of $\Delta n(N)$ are positive in systems, I, III, and V, where $\frac{M_1}{d_1} \gg \frac{M_2}{d_2}$, and negative in systems II, IV, and VI, where $\frac{M_1}{d_1} \ll \frac{M_2}{d_2}$.

The smallest deviations from additivity in all the cases studied are observed when the concentrations are expressed in volume fractions, corresponding to additivity rule (2.9). Unlike $\Delta n(N)$ and $\Delta n(P)$ the deviations from additivity $\Delta n(V)$ are not connected with relationships (2.24–2.29), and are caused by deviations from ideal behaviour, as shown, in particular, by the change in volume on mixing. The fact that $\Delta n(V)$ is independent of the relationship between the properties of the components is shown very clearly by a comparison of the carbon tetrachloride–2,2,4-trimethylpentane and bromobenzene–2,2,4-trimethylpentane systems. Both systems represent Case II (2.25), and accordingly the $\Delta n(N)$ and $\Delta n(P)$ curves are disposed in exactly analogous fashion. In the first system, where expansion is observed, the $\Delta n(V)$ values are negative, but in the second, where contraction is observed, they are positive.

III. RELATIONSHIP BETWEEN THE DEVIATIONS FROM ADDITIVITY OF REFRACTIVE INDICES, DENSITIES, AND SPECIFIC REFRACTIONS

The above relationship between the deviations from additivity $\Delta n(V)$ and the change in volume is obvious from a physical point of view; the refractive index depends on the number of particles in unit volume and is thus affected by expansion and contraction in the system. This relationship must be studied in more detail when examining the possibility of characterising the behaviour of the components of solutions by the values of $\Delta n(V)$.

The deviations of the refractive indices from additivity in all organic systems (with the exception of a few rational ones) do not exceed 1.0–1.7% of n, and the change in volume

likewise does not exceed a few per cent, so that in order to find the desired relationship we are justified in differentiating the general expression for the specific refraction (2.1) and replacing the differentials by finite increments. In the general case, where the system is non-ideal and deviations of the specific refraction from additivity and volume changes both occur, we have

$$\Delta f(n) = r\Delta d + d\Delta r. \qquad (3.1)$$

When the Gladstone–Dale formula $f(n) = n-1$ is used as a particular case of (3.1), we obtain

$$\Delta n = r\Delta d + d\Delta r. \qquad (3.2)$$

Here, of course, the deviations from additivity Δn, Δd, and Δr signify the deviations from rules which have a physical basis and not from arbitrary ones, i.e. the quantities $\Delta n(V)$, $\Delta d(V)$, and $\Delta r(P)$, so that a more correct form of (3.2) is

$$\Delta n(V) = r\Delta d(V) + d\Delta r(P), \qquad (3.3)$$

where $r = (n-1)/d$.

The particular expression (3.3) is just as rigorous as the general expression (3.1). The approximate character of the Gladstone–Dale equation is shown only in that the quantity Δr in (3.3) includes two effects: the deviations from additivity resulting from the non-ideal nature of the system and the deviations resulting from the inaccuracy of the Gladstone–Dale function. The simple relationship (3.3) makes it possible to reach a number of extremely important conclusions about the reasons for deviations from additivity of refractive indices and the connection between these and physical and chemical processes in solution.

Firstly, it can be seen from (3.3) that there need not necessarily be a simple relationship between the deviations from additivity of the refractive indices and the densities, as claimed by Pulfrich[67] and by a number of authors, up to the present. The sign of $\Delta n(V)$ is determined by the sign of the volume change $\Delta v = -\Delta d/d^2$ only when Δr is sufficiently small and

$$|d\Delta r| < |r\Delta d|. \qquad (3.4)$$

Condition (3.4) is in fact observed in normal systems, and in a large number of systems with associated and interacting components. In systems with contraction, therefore, $\Delta n(V)$ is usually positive, and in systems with expansion, negative*. This is not a strict rule, however, and when condition (3.4) is not fulfilled, cases are possible where compression is accompanied by negative deviations $\Delta n(V)$, and expansion by positive deviations. This has been confirmed experimentally in a number of cases, some of which are dealt with below in connection with the problem of characterising interaction between components from the sign of $\Delta n(V)$.

A very important consequence of relationship (3.3) is that there is no definite relationship between the sign of $\Delta n(V)$ and the nature of the interaction between the components. Positive deviations $\Delta d(V)$ are not always associated with compound formation, and negative deviations $\Delta d(V)$ are not necessarily due to dissociation of associated components[14]. A change in volume may also be observed when normal liquids, which do not interact chemically, are mixed, owing to the inequality of the internal pressures and compressibility coefficients of the components[84], and also to the purely geometrical effect of packing particles of different size and shape.

On the other hand, the deviations from additivity of the refraction $\Delta r(P)$ or $\Delta Mr(N)$ when chemical compounds are formed in a system need not necessarily be positive. For example, the molecular compounds formed by phenols with aromatic amines show a depression of the molecular refraction[85].

These considerations indicate that, contrary to the views of earlier workers, negative refractive-index isotherms may also be expected in systems with clearly defined chemical interaction between the components. Negative deviations from additivity of the refractive indices may be brought about by the compound formation itself, and not as a result of the erroneous formulation of the additivity rule (as in papers by Matavul' [30,40]), nor by the opposite effect of the breakdown of associated molecules. This assertion requires experimental confirmation.

An examination of the literature data for a large number (over 150) binary systems, together with our experiments on systems not previously studied, has shown that negative $n(V)$ curves are in fact encountered in typical irrational systems, such as mixtures of dimethylaniline with acids (formic, isobutyric, and isovaleric) and with *m*-cresol. The results for three of these systems are given in Fig. 4, and show the reasons for the appearance of negative $n(V)$ isotherms. In all three cases, as is usual in irrational systems, contraction takes place $[\Delta d(V) > 0]$. With this condition, in accordance with (3.3), negative values of $\Delta n(V)$ can only be observed if $\Delta r < 0$ and $|r\Delta d| < |d\Delta r|$, and these conditions apply in the systems under study. The marked negative deviations Δr, to which the appearance of negative $n(V)$ isotherms is here related, result directly from chemical interaction of the components. As already mentioned, the formation of molecular compounds by aromatic amines with phenols shows a decrease in molecular refraction compared with the additive values[85]. This depression is related to the hypsochromic shift of the absorption bands of the amines under the influence of acids. In the light of modern views on the relationship between molecular refraction and electronic spectra on the one hand, and the structure of organic substances on the other, these effects shown by aromatic amines are quite understandable. The p-π-conjugated system in aromatic amines, which is associated with exaltation of the refraction and bathochromic

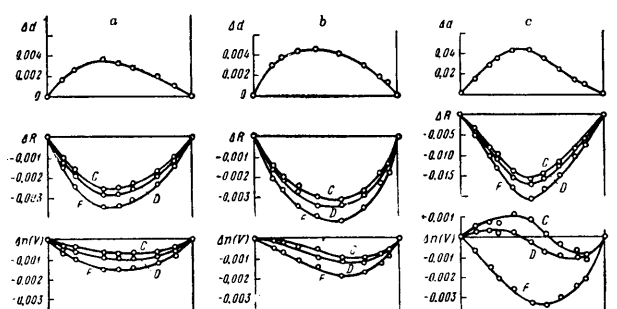
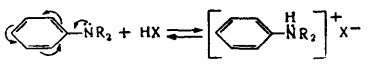


Fig. 4. Negative deviations from additivity of the refractive indices $\Delta n(V)$ molecular refractions ΔR, and densities Δd in the irrational systems (*a*) dimethylaniline–*m*-cresol, (*b*) dimethylaniline–isovaleric acid, and (*c*) dimethylaniline–formic acid, for red (*C*), yellow (*D*), and blue (*F*) light.

* We are here dealing with the quantities $\Delta n(V)$. The deviations $\Delta n(N)$ and $\Delta n(P)$ are not, generally speaking, related to the volume change in a simple fashion. Attempts to affirm such relationships [63,70] are not justified.

shifts of the absorption bands, is destroyed when protons are introduced into the electron clouds of the nitrogen atom. The polarisability of the electrons, in the field of the positive charge, decreases, leading to a hypsochromic shift of the long-wave absorption bands and to marked negative deviations from additivity of the molecular (or specific) refraction:



The above interpretation of the appearance of negative $n(V)$ isotherms in irrational systems is supported by a comparison of mixtures with different amines. The Table gives the maximum (absolute) values of $\Delta n(V)$ for 9 systems of the amine–acid type, and shows that the systems with aniline have large positive $\Delta n(V)$, characteristic of systems involving compound formation. In the methylaniline systems the deviations $\Delta n(V)$ are much smaller, and the $n(V)$ isotherms, although positive, cannot be distinguished from those for normal ones [76]. Finally, in the dimethylaniline systems, the sign of the $n(V)$curves becomes "anomalous" and they are now convex towards the composition axis. The strength of the bases increases in the series: aniline, methylaniline, dimethylaniline, and the degree of association apparently decreases in the same order: the hydrogen bond, which is a factor in association, is absent in dimethylaniline. If therefore we start from the original assumption [14] that compound formation is revealed in positive deviations from additivity (which increase with increase in the strength of the interaction) while breakdown of associated components leads to the opposite effect, then we would expect effects exactly opposite to those actually observed. From the modern viewpoint, the relationships observed in these systems are quite understandable. As a direct consequence of compound formation, the negative deviations appear in mixtures containing the strongest base, dimethylaniline; moreover, this has the greatest exaltation of molecular refraction, which decreases on salt formation. In the case of the weaker base methylaniline, the Δr are smaller and the effect of the contraction predominates.

Maximum (absolute) deviations of the refractive indices from additivity in mixtures of aromatic amines with acids.

Base	Maximum values of $\Delta n_D^{20}(V) \times 10^4$ in systems with the acids		
	formic	iso-butyric	iso-valeric
Aniline	+218	+78	+76
Methylaniline	+46	+27	+30
Dimethylaniline	+2 * / −111	−17	−11

* $n_D^{20}(V)$ isotherm positive-negative (Fig. 4).

The dimethylaniline–formic acid system is of particular interest, since here the shape of the refractive-index curves depends on the wave-length of the light. The deviations of r from additivity observed in this case increase on going from the red to the violet region of the spectrum, and are related to the hypsochromic shift of the absorption bands in the near ultra-violet, which is observed on interaction with acids. For the red C rays, at a considerable distance from the violet, the deviation of r from additivity is comparatively

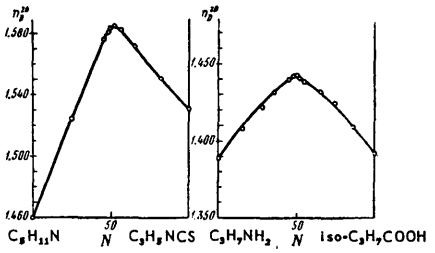


Fig. 5. Examples of singular diagrams for refractive index (piperidine-allyl mustard oil [10] and propylamine-isobutyric acid [31]).

small; the opposite effect of contraction predominates over a wide concentration range, and the $n_C^{20}(V)$ curve is S-shaped, with a change in sign. For the yellow D rays, an exactly analogous picture is obtained, but as a result of the increase in Δr, the negative part of the $n_D^{20}(V)$ curve increases considerably. For the blue F lines, the values of Δr are so high that the $n_F^{20}(V)$ curve is negative at all concentrations and indistinguishable from the analogous curves for mixtures of non-interacting components.

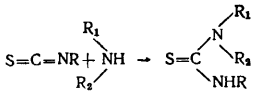
There is thus no simple relationship between the nature of the interaction of the components and the magnitude of the deviations from additivity $\Delta n(V)$. Similarly, in accordance with (3.3), no strict correspondence can be expected between the signs of $\Delta n(V)$, $\Delta r(P)$, $\Delta d(V)$, or $\Delta v(P)$.

IV. UNIQUE POINTS ON REFRACTIVE-INDEX DIAGRAMS

In physicochemical analysis, the unique points on the composition vs. property diagrams are used, in addition to deviations from additivity, to examine the interaction between the components of binary and more complex systems. Until recently, the only kinds of unique point which have figured in work on the refractometric method of physicochemical analysis have been singular points and maximum turning points.

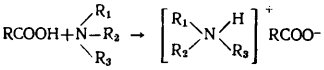
The singular (Daltonide) points have been most studied. These appear when a stable compound, not dissociated into its components, is formed in the system, and they correspond exactly to the composition of the compound. Neither the position of the singular point, nor the very fact of its existence, are dependent on the method of expressing the composition. The singular points so far observed in binary organic systems have been the so-called *angular* points, i.e. points of intersection of two branches of the curve (Fig. 5).

The number of different types of binary systems with a singular point on the refractive-index curves which have been studied is small, all being systems with interaction of the type $A + B = C$. A favourite example of such "rational" organic systems in papers by Kurnakov's school was the combination of primary or secondary amines with isothiocyanates, in which stable (practically undissociated) substituted thioureas, with a marked tendency to undergo supercooling, are formed, even in the cold:



Other examples include certain systems of the aliphatic

amine–carboxylic acid type, in which low-melting substituted ammonium salts, also with a tendency to supercooling, are formed[31,33]:



(R_1 and R_2 = H or alkyl; R and R_3 = alkyl)

Singular refractive-index diagrams for binary systems are of interest chiefly as illustrative material for characterising particular features of composition vs. property diagrams. In organic chemistry, the singular refractive-index curves so far studied have been of little value: the formation of thioureas and substituted ammonium salts are well-known and typical amine reactions.

The maxima on the refractive-index curves were the first unique points to which attention was turned in connection with interaction between components[1], and their appearance was taken as proof of compound formation. The position of the maximum was sometimes taken to correspond to the composition of the compound formed[86], although there were also reports that the maxima of n were displaced considerably towards the component with the higher index and should not be used to deduce the composition of the compound. Although refractive-index maxima have long been known, the conditions for their appearance were examined only recently[74]. The other forms of unique point on the refractive-index isotherms — minimum points and points of inflection — have likewise only been studied in recent years[73,75].

Let us first examine in a general way the conditions for the appearance of maxima and minima in the refractive index. For deviations from additivity of the $f(n)$ function, (2.8), we have the expression

$$\Delta f(n) = f(n)_{exp} - f(n_1)V_1 - f(n_2)V_2 \quad . \qquad (4.1)$$

The conditions for turning points of $f(n)$ are obtained by differentiating with respect to V_1 and equating $\partial f(n)/\partial V_1$ to zero:

$$\frac{\partial}{\partial V_1}\Delta f(n) = f(n_2) - f(n_1) \quad . \qquad (4.2)$$

This equation is the condition for maximum and minimum values of $f(n)$, but we are interested in the maximum and minimum values on the n isotherms. In order to solve this problem, it is not necessary to choose the best of the proposed molecular (or specific) refraction formulae, since the derivative $\partial f(n)/\partial n$ does not become equal to zero under any set of real conditions, for any of the forms of the function $f(n)$ (2.2–2.5) or for any other proposed refraction formula. Consequently, $\partial f(n)/\partial V = 0$ only when $\partial n/\partial V = 0$. Thus the maximum and minimum values of $f(n)$ must correspond to maximum and minimum values of n, and, if condition (4.2) is fulfilled, maxima or minima should be observed on the refractive-index curves.

Condition (4.2) requires only a definite relationship between the numerical values of the refractive indices of the components n_1 and n_2 and the magnitude of the derivative of the deviation from additivity $\frac{\partial}{\partial V_1}\Delta f(n)$. It contains no limitations associated with the reasons for the deviation from additivity, $\Delta f(n)$. But these deviations from additivity (see 4.1) need not be related to the production of new molecules in the system, and may be due to purely physical (or even geometrical) effects of change in volume. From this it follows that refractive-index maxima and minima may also be obtained in systems without chemical interaction or dissociation of the components, for certain definite numerical relationships between the properties of the components (n, r) and the volume change of the system.

An approximate rule defining the conditions for the appearance of maximum and minimum values of n, and their position, may be obtained using the Gladstone–Dale function (2.2), which satisfies the requirements of additivity satisfactorily; considering the simplest case, where the dependence of the refractive index on the concentration approximates to the parabolic equation $n = a + bV + cV^2$, we have

$$\Delta n(V) = KV_1(1 - V_1) \quad , \qquad (4.3)$$

where K is a constant for a given system.

In this case (4.2) becomes

$$V_e = \frac{1}{2} + \frac{n_1 - n_2}{2K} \quad , \qquad (4.4)$$

where V_e is the concentration of the first component corresponding to an extremal value of n, and n_1 and n_2 are the refractive indices of the components. In normal systems, where condition (3.4) is fulfilled, the sign of the constant K will be determined by the change in volume of the system. If $K > 0$ (contraction), there will be a maximum, and when $K < 0$ (expansion), a minimum refractive index in the system.

Relationship (4.4) shows that for a given value of K, a maximum value of n will lie closer to the component with larger n, and a minimum value closer to the component with smaller n, by an amount which increases with the difference between the refractive indices of the components.

Taking account of the obvious relationship $0 < V_e < 1$, we find that in case (4.3), the condition for the appearance of maxima or minima of n is

$$|n_1 - n_2| < |K|. \qquad (4.5)$$

Examination of the experimental refractive-index data and volume changes for normal systems indicates that K may amount to 0.02. It may thus be expected that maxima or minima in n will appear in normal systems when the refractive indices of the components are sufficiently close: $|n_1 - n_2| < 0.02$.

On the basis of these considerations, it has been possible to detect extremal values of the refractive index in mixtures of hydrocarbons and their halogen derivatives, which are usually included in the class of normal systems[74]. The cyclohexyl bromide–ethylbenzene system has been most studied and illustrates clearly the rule formulated above for the dependence of the displacement of the maxima or minima on the relationship between the properties (refractive indices) on the components. Cyclohexyl bromide and ethylbenzene have widely differing dispersions, so that the difference $n_1 - n_2$ depends to a marked extent on the wavelength: the value for the C lines is 15 times, and that for the F lines 33 times greater than that for the D lines, while for red light, ethylbenzene has the lower n, and for blue, cyclohexyl bromide (Fig. 6). At the same time the value of K (4.3) varies little with wavelength. In accordance with (4.4), the minimum on the n_D^{20} isotherm at 43 vol.% of ethylbenzene is displaced towards ethylbenzene (66%) on the n_C^{20} isotherm, and towards cyclohexyl bromide (10% $C_6H_5C_2H_5$) on the n_F^{20} isotherm. At shorter wavelengths, $n_1 - n_2$ will be even larger and the minimum in n in this system probably disappears.

Comparison of the 15 systems with minimum n known at present [73,74] shows that they contain both strongly associated components (acids and alcohols) and weakly associated or non-associated components (hydrocarbons and their halogen derivatives). Neither the existence of the minimum n, nor its position, nor its value, can be related to the concentration of associated components or to their degree of association. From this it follows that negative deviations of n from additivity (for any formulation) need not be related to dissociation of the components.

Points of inflection are the least studied of the unique points on composition vs. property diagrams. They are most frequently observed on heats of mixing and viscosity curves, in systems with fairly well defined chemical interaction between the components. Their appearance on the diagrams for these properties is usually interpreted as resulting from the formation of compounds of the associated components [13,14]. Unlike singular and turning (extremal) points, points of inflection on property vs. composition curves may appear or disappear according to the method of expressing the composition [14], so that in discussing points of inflection, the choice of the correct method of expressing the composition is of fundamental importance.

Points of inflection on the $n(V)$ isotherms were first considered for the case of S-shaped curves with a change in sign of the deviations from additivity [73,75]. The conditions for the appearance of positive–negative $n(V)$ isotherms may be sufficiently revealed by starting from the expression for the deviations of the refractive index from additivity (3.2):

$$\Delta n(V) = r\Delta d + d\Delta r.$$

Since Δr and $d\Delta r$ are not very large compared with $r\Delta d$, two cases are of practical interest: 1) those where the deviations of the specific refraction from additivity are practically zero; 2) those where the terms $r\Delta d$ and $d\Delta r$ are of the same order of magnitude.

In the first case, as pointed out in the previous section, the sign of $\Delta n(V)$ should be the same as that of the deviations of the densities from additivity and opposite to that of the change in volume, so that in systems where the condition of additivity of r is sufficiently well fulfilled, positive–negative $n(V)$ isotherms can and should appear only when the sign of Δd and Δv changes as the concentration of the components changes.

In the second (more general) case, a change in the sign of $\Delta n(V)$ is obviously possible in systems where the $d(V)$ or $v(P)$ isotherms do not change sign. A necessary condition is that the signs of Δr and Δd should not be the same (or that those of Δr and Δv should be). This condition is not sufficient, however, since it is also necessary that in one concentration range $|r\Delta d| > |d\Delta r|$ and in another $|r\Delta d| < |d\Delta r|$. This last requirement is satisfied when the values of d or r for the components differ appreciably, the greater density corresponding to the lower refraction. These conditions restrict considerably the number of systems in which positive–negative $n(V)$ curves may be expected, and such curves are rare. It has been possible, however, to confirm experimentally all three of the above possibilities for the production of positive–negative $n(V)$ isotherms, and these are shown in Fig. 7.[75]

The case of S-shaped isotherms in systems with contraction at all concentrations and with marked negative deviations of r from additivity is comparatively more common. It is normally found in irrational systems of the

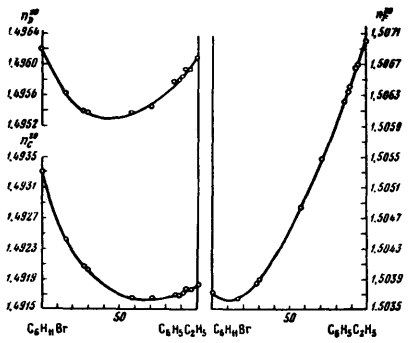


Fig. 6. Position of the refractive-index minima in the ethylbenzene–cyclohexyl bromide system for red (C), yellow (D), and blue (F) light.

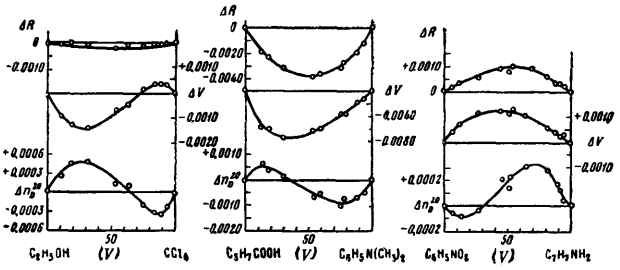


Fig. 7. Three cases of positive-negative $n(V)$ isotherm formation (ethyl alcohol–carbon tetrachloride, dimethylaniline–butyric acid and m-toluidine–nitrobenzene systems).

acid-base type, with aromatic or heterocyclic bases showing marked absorption in the near ultraviolet. Positive–negative $n(V)$ isotherms are encountered not only in irrational systems [75], however, so that points of inflection on the n curves cannot be regarded as sufficient evidence for the formation of compounds in a system.

V. CLASSIFICATION OF REFRACTIVE-INDEX ISOTHERMS

The classification of refractive-index isotherms proposed by Anosov [12–14] assumes that the composition is expressed in mole fractions (percentages). The incorrect choice of this parameter is one of the fundamental reasons for the inapplicability of this classification and its non-correspondence (except for the 4th class of singular diagrams) with observed relationships.

Another reason for the unsuitability of Anosov's classification is the erroneous assumption that the magnitude of the deviations from additivity depends unequivocally on the nature of the behaviour of the components (for example, compound formation could be accompanied only by positive deviations from additivity).

A third reason for errors made in the past in interpreting the shape of the refractive-index isotherms is the complete neglect of all factors influencing the deviations of the refractive index from additivity except the purely chemical

ones. Any deviation from additivity (erroneously formulated, moreover) was ascribed to the production of new molecules in the system and related either to combination of the components or to breakdown of associated molecules to simpler forms.

The new classification of refractive-index diagrams [72] for the physicochemical analysis of binary systems is based on the conclusions given in the previous sections regarding the shape of the refractive-index curves and on the results of examination of the experimental data for almost 200 organic systems.

The classification of all non-singular curves is based on the magnitude of the deviations from additivity with respect to the *volume* fractions of the components, $\Delta n(V)$. Since the earlier qualitative approach to the characterisation of non-singular curves by the direction of their convexity (the sign of the deviations from additivity) is clearly insufficient for any definite differentiation of systems according to their physicochemical character, it is necessary to use some quantitative criterion, such as the roughly quantitative deviations from additivity, as one of the factors for classification.

Examination of the available data shows that in normal systems, and in systems with associated components which do not form compounds, the maximum deviations of the refractive indices from additivity do not exceed +0.007. Higher positive values of $\Delta n(V)$ are encountered only in systems with clearly defined chemical interaction between the components, so that high values of $\Delta n(V)$, greater 0.007, may be taken as fairly conclusive evidence for classifying the system as irrational, in spite of the somewhat arbitrary and approximate nature of this criterion.

It is not possible to find an analogous criterion to detect association of the components. It is evident that even the marked association of components resulting from hydrogen bonding is not reflected distinctly in the refractive-index curves. This conclusion is in accordance with the failure of attempts to detect hydrogen bonds in binary systems containing alcohols and acids from the deviations from additivity of the molecular refractions [87-89].

According to the conclusions of the previous section, the only forms of unique point which may be used as criteria for the formation of compounds are singular points and maximum turning points. The actual existence of a non-singular maximum is proof of compound formation only when the difference between the refractive indices of the components is sufficiently high, i.e. $n_1 - n_2 > 0.02-0.03$; otherwise systems should be classed as irrational not on the basis that a maximum n exists, but on the height of this maximum, i.e. on the value of the maximum deviation from additivity.

For the purposes of physicochemical analysis, therefore, three classes of $n(V)$ curve should be distinguished:

Class I -- isotherms with a small curvature: maximum values of $\Delta n(V)$ positive or negative, but not exceeding +0.007.

Class II — isotherms with a marked convexity away from the composition axis (deviations from additivity $\Delta n(V)$ exceeding 0.007).

Class III — isotherms with a singular point (break), characteristic of systems in which non-dissociated compounds are formed. Since the singular points are preserved on going from mole fractions to volume fractions, this class corresponds exactly to Anosov's Class 4.

Most binary liquid systems have $n(V)$ isotherms of type I, including all normal systems, systems with non-interacting associated components, and also a number of systems with chemical interaction, sometimes fairly strong, but not revealed distinctly on the $n(V)$ curves. Isotherms of Class I may show points of inflection, and possibly maximum or minimum turning points (when the refractive indices of the components are similar, i.e. $n_1 - n_2 < 0.02$).

Class II includes systems with marked chemical interaction and formation of partly dissociated compounds. The isotherms for this class quite often show maxima, and occasionally points of inflection*.

The singular points on Class III diagrams, in almost all known cases, are maximum turning points. Other unique points may be encountered, but only one such case is known — the non-singular maximum in the acetic anhydride—-water system.

This classification includes all available literature data on refraction in binary liquid systems.

VI. THE USE OF REFRACTOMETRY FOR THE STUDY OF INTERACTION BETWEEN COMPONENTS IN BINARY LIQUID SYSTEMS

According to the new classification, it is necessary to distinguish cases where the refractometric data, by themselves, give sufficient proof of compound formation between the components (curves of Classes II and III), from cases where such data alone cannot give definite information regarding the behaviour of the components (curves of Class I). Unfortunately, Class I is the most widespread, and this restricts the independent application of refractometry in physicochemical analysis. Other methods must be used to study systems where the deviations of the refractive indices from additivity are small. In this case, however, we must not restrict ourselves to the traditional comparison of the shape of the property vs. composition curves with isotherm types established empirically, but should examine, in all possible detail, the quantitative relationships between the various properties. An example of such a relationship is Eqn. (3.3), and use of this in the study of curves of Class I reveals, in particular, typical irrational systems in which compound formation is not clearly reflected in the refractive-index curves, as a result of the opposed signs and mutually weakening effects of the non-additivity of the densities and specific refractions.

When the compounds formed are very unstable and their concentrations very low, they can hardly be detected by the refractometric method, for the influence of the negligibly small number of new molecules formed will not be noticed against the other effects. An example is the tetranitromethane–benzene system [77]. When the components are mixed, a fairly intense yellow colour appears and the spectrophotometric curves give distinct proof of the formation of new molecules, although the refractive-index diagrams show no signs of interaction between the components, in spite of the close connection between the refraction and absorption of light. In view of the low concentration of unstable complexes formed, the factor determining the shape of the

* The single case recently described [90] of a refractive-index minimum existing together with a fairly high maximum (in the acetic anhydride – nitric acid system) requires confirmation and explanation.

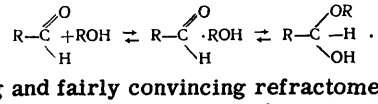
$n(V)$ isotherms is not the deepening of the colour, but the expansion observed in the system.

The position of the singular points or the maximum deviations from additivity (on curves of Class II) can be used to obtain information about the composition of the compounds formed. It must be noted, however, that the position of these points is determined, strictly speaking, not by the composition of the compounds but by the ratio of the stoichiometric coefficients of the equations for the chemical processes taking place in the system. Thus, for example, a singular point may be found at a molar ratio of components of 1 : 1 in combination reactions $A + B = C$ and also in double decomposition reactions $A + B = C + D$. Information on the composition of the compounds may thus be obtained from the position of the singular points or maximum $\Delta n(V)$ if further information is available, or assumptions made, regarding the type of reaction occurring in the system.

The new viewpoint is well based on a more careful interpretation of refractometric data. Recent views [71-79] differ essentially from the basic postulates of earlier work and in many cases lead to a different interpretation and evaluation of the shape of non-singular refractive-index diagrams. Since the many earlier attempts to relate the deviations from additivity $\Delta n(N)$ and $\Delta n(P)$ only to interaction or dissociation of components with different molar volumes and densities must be regarded as fundamentally erroneous, it becomes necessary to re-examine the conclusions reached in earlier work by interpreting $\Delta n(N)$ and $\Delta n(P)$ in this manner*.

As pointed out in Section II, certain conclusions reached by early workers, such as those of Matavul' [30,32] and Aleksandrov [47] regarding the influence of association on the refractive index, are quite incorrect. Certain early data on compound formation in organic systems appear unconvincing when re-examined from the new viewpoint. For example, the data for mixtures of acetone with carboxylic acids [64] cannot be taken as proof of compound formation; another example is the small maximum n_D in the pyrrole–pyridine system [96], where the values of n for the components are similar ($n_1 - n_2 = 0.0013$), which is inadequate to prove that a compound is formed, without the support of other data.

At the same time many of the conclusions reached in earlier work, relating to systems with clearly defined chemical interaction between the components, retain their significance. For example, refractometry has played an important part in solving the problem of hemiacetal formation in aldehyde–alcohol mixtures [5,69,97-99]. Measurement of the change in refractive index with time for these systems not only proves that hemiacetal formation takes place, but also reveals the two-stage mechanism of the process:



Interesting and fairly convincing refractometric data have been obtained for the reaction of acetic acid and its nearest homologues with strong acids (sulphuric, phosphoric, and nitric), in which the carboxylic acids act as bases [35,36,40,41,51].

Most observations on the reactions of amines with phenols and carboxylic acids retain their significance.

The formation of hydrates of organic compounds in many aqueous solutions is also being studied by means of refractive-index curves. In this case, however, the $n(N)$ diagrams previously used give a very distorted, if not always completely erroneous, picture of hydrate formation. Since the molecular volume of water is much smaller than that of organic compounds, the deviations from additivity $\Delta n(N)$ acquire extremely high values which do not correspond to the actual hydration effect.

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In summing-up the discussion of the principles involved in applying refractometry to the study of interaction between the components of liquid systems, we may consider its future prospects. Refractometry is not one of the most sensitivie methods for studying intermolecular interactions, and reveals only comparatively strong interactions where fairly stable compounds are formed. In studying systems where such interaction takes place, refractometry may be extremely useful, and equal in importance to other methods. Since the method is readily available, technically simple, and highly accurate, its use in this field is very convenient. In the present state of our knowledge of specific and molecular refraction, however, refractometry must be regarded as poorly adapted to the study of interactions not accompanied by a marked change in the structure and polarisability of a large number of molecules.

Recognition of these features of the refractometric method should prevent the repetition of earlier mistakes and the publication of inconclusive arguments.

* After the publication of articles [71, 72] drawing attention to the inapplicability of the existing classification of refractive-index diagrams and the $n(N)$ additivity rule, a number of authors [41–45, 91] recognised the need to re-examine the earlier conclusions and went over to the study of $n(V)$ curves. Some recent papers [92–95], however, still deal with $n(N)$ curves from the old point of view.

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THE AROMATIC BOND AND SOME PROBLEMS OF THE STRUCTURE OF AROMATIC COMPOUNDS

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INTRODUCTION

The formula proposed by Kekulé[1,2] for benzene, with alternating double and single bonds, explained many but not all its properties. This formula made it difficult to understand, for example, the specific type of reactivity shown by benzene and the existence of one instead of two *ortho*-isomers[3,4].



For this reason Kekulé later suggested[5] that the double bonds in the benzene ring are not fixed but mobile, i.e. they oscillate rapidly, moving around the ring.

The concept of the oscillation of double bonds as an important distinguishing feature of aromatic compounds was accepted rapidly and held sway for a long time. In subsequent papers it was developed into an orderly system of ideas[6]. This concept explained in particular the identity of the two *ortho*-positions in monosubstituted benzenes. In polysubstituted benzenes and especially in di- and polycyclic aromatic compounds, however, the *ortho*-positions are not equivalent, one being more reactive than the other. This led to the suggestion that in these compounds the possible oscillatory forms possess different stabilities, and therefore, being in dynamic equilibrium, take part to different extents in reaction[7]. Thus the double bonds of such compounds are partly or even completely fixed[8-11].

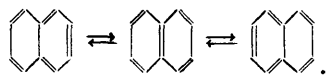
From the progress made in recent years in the study of the fine structure of aromatic compounds it may be concluded that there can be neither oscillation nor complete fixation of the bonds in aromatic molecules.

It has been established by numerous methods that the structure of the benzene molecule is a regular hexagon in which the six π electrons of the carbon atoms do not interact in pairs but as a single sextet. Therefore, all the C – C bonds of benzene are completely equivalent and differ in electron density both from single and from double bonds. From this point of view, Thiele's theory of partial valencies[12] represents the actual structure of aromatic substances better than Kekulé's concept of oscillating bonds. However, many experimental facts indicate that in aromatic compounds other than benzene the C – C bonds are not identical; some of them possess greater electron density, or have greater "double-bond character", than others.

The complete equivalence of the C – C bonds characteristic of the benzene molecule contrasts with the state of these bonds in its derivatives, e.g. di- and polycyclic aromatic compounds. Therefore, it is possible to consider that substituent groups or condensed rings upset to some extent the equivalence of the bonds.

PARTIAL BOND FIXATION

The non-equivalence of the bonds in aromatic compounds was first studied in the case of naphthalene. By analogy with the Kekulé dynamic structure for benzene, the naphthalene molecule can be represented by dynamic formulae[13,14], on the basis of which it might be supposed that the bonds in naphthalene would be equivalent:



However, many observations indicate the great difference in properties between the 1 – 2 and 2 – 3 bonds. For the sake of clarity, these observations are classified below according to the types of reactions studied.

Cyclisation Reactions and Reactions Occurring via the Intermediate Formation of Rings

As early as 1893 Markwald[15-17] noted the considerable reactivity of one of the two *ortho*-positions in β-naphthol and β-naphthylamine. Thus, when the Skraup reaction is carried out with β-naphthylamine, only the angular benzoquinoline (I) is obtained. In a number of cases formation of I is accompanied by displacement of a substituent present in position 1 of the 2-naphthylamine molecule. According to