TABLE 3.

	0.25	0.50	0.75
L	0.562	0.578	0.664
η_{add}	0.569	0.892	1.214
η_{calc}	0.320	0.516	0.806
η_{exp}*	0.322	0.500	0.822
Relative error, %	1	3.2	2.0

* The values of η_{exp} were found graphically because Udovenko and Airapetova[8] did not give data for mole fractions of 0.25, 0.50, and 0.75.

Eqns. (5) are valid for $S \leq 10$; at higher values of S the calculation should be made by Eqns. (4). Two examples of the calculation of the viscosity isotherm by the proposed method are given below.

Example 1. The ethyl benzoate–benzyl benzoate system[7]: $\eta_1 = 8.518$; $\eta_2 = 2.014$; $S = 4.229$. From Eqns. (4) we find the values of L: $L_{0.25} = 0.805$; $L_{0.50} = 0.816$; $L_{0.75} = 0.871$. The values of η_{add} for the corresponding mixtures are as follows: $\eta_{0.25\,add} = 3.640$; $\eta_{0.50\,add} = 5.266$; $\eta_{0.75\,add} = 6.892$. From the products $L_i \eta_{i\,add} = \eta_{i\,calc}$ we can find the corresponding values of η_{calc}: $\eta_{0.25\,calc} = 2.930$; $\eta_{0.50\,calc} = 4.264$; $\eta_{0.75\,calc} = 6.003$. The experimental viscosities of the mixtures are as follows: $\eta_{0.25\,exp} = 2.92$ (obtained graphically); $\eta_{0.50\,exp} = 4.307$; $\eta_{0.50\,exp} = 6.109$. The percentage errors are respectively 0.3, 1.0, and 1.6.

Example 2. The formic acid–ethyl ether system[8]: $\eta_1 = 1.537$; $\eta_2 = 0.246$; $S = 6.248$. The values of L were found from Eqns. (5), the results being given in Table 3.

Good agreement with experiment is also obtained when several isotherms for the same system are calculated.

The proposed method of calculation makes it possible to evaluate graphically the shape of the viscosity isotherms of binary systems with non-interacting components, in most cases with a relative error not greater than 5%, which is a little more than the usual error in the determination of viscosity (±2–3%). Clearly, the accuracy of the calculation could be improved if the treatment were confined to $L_i - S$ curves for groups of chemically related systems (for example, hydrocarbon–hydrocarbon; alcohol–hydrocarbon, acid–halogenomethane systems, etc.). However, the proposed method of calculation would whilst gaining in accuracy lose in generality of application, which would make it less suitable for the interpretation of viscosity diagrams for systems with chemical interaction — the ultimate aim of the present investigation.

The method does not describe the viscosity isotherms with a minimum. However, the total number of binary systems having isotherms with a minimum is small and as a rule the "overhang" of the isotherm resulting in a minimum rarely exceeds 5–7% of the calculated value of the viscosity.

The author thanks G. I. Yanchuk for help with the calculations.

SUMMARY

1. A study has been made of the shape of the viscosity isotherms of 100 binary systems with non-interacting components, relative to the straight line $\eta = x_1(\eta_1 - \eta_2) + \eta_2$, the composition x_1 being expressed in mole fractions.
2. The L–composition ($L = \eta_{exp}/\eta_{add}$) curves have been calculated for all the systems.
3. The shape of the viscosity isotherms depends on the value of the ratio of the viscosities of the initial components $S = \eta_1/\eta_2$. With increase in S the position of L_{min} shifts towards mixtures rich in the less viscous component.
4. The values of L for mixtures of a given composition steadily decrease with increase in S. An expression has been derived for the variation of L with S for mixtures in which the mole fraction of the more viscous component is 0.25, 0.50, and 0.75.
5. On the basis of the expressions derived, a method has been proposed for the calculation of the viscosity isotherms of binary systems with non-interacting components.

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REDUCTION OF ANIONS IN THE PRESENCE OF SMALL AMOUNTS OF LANTHANUM IONS AT A DROPPING MERCURY CATHODE

Liu Shou-jung and S. I. Zhdanov

Data have been given[1] on the action of small amounts of the highly charged La^{3+} cations on the reduction of the nitrate anion present in high concentration. This system, which is unusual in polarography, exhibits phenomena indicating that the structure of the electrical double layer has a substantial influence, uncomplicated by diffusion of a depolariser, on the kinetics of the electrode process.

EXPERIMENTAL

All measurements were made on the visual instrument described in Ref. 2. The glass cell was placed in an air thermostat at 25° ± 0.1°. The characteristics of the capillary were $m = 2.3$ mg sec^{-1} and $\tau = 4.2$ sec (in 0.1 M KNO_3 at $h = 30$ cm Hg and $\varphi = 0$). Under these conditions second-order maxima were excluded, as was shown by a separate experiment. Solutions were made up with twice distilled water. Reagents were usually further purified by recrystallisation from twice distilled water and by heating. Air was displaced from the solutions and the cell with purified hydrogen obtained by the electrolysis of water. The potential of the dropping mercury electrode was measured relative to the normal calomel electrode using a Luggin capillary.

Results

Fig. 1 shows polarisation curves of 0.1 M potassium nitrate solutions containing small quantities of lanthanum chloride. In the absence of lanthanum ions reduction of nitrate ions begins at -1.55 V (Fig. 1, curve *2*). Addition of lanthanum chloride considerably accelerates the process. Thus in the presence of 2×10^{-4} M lanthanum chloride the same current (for example 10 μA) is reached at a potential which is almost 0.5 V less negative than in the absence of lanthanum chloride. In 0.01 M potassium nitrate solution this shift is ~0.7 V, whereas in 1 M KNO_3 it is only 0.35 V. At low lanthanum chloride concentrations potassium nitrate has a smooth polarisation curve. In the presence of 4×10^{-4} M lanthanum chloride a nitrate-ion wave with a characteristic minimum appears. With further rise in the lanthanum chloride concentration this wave grows, the minimum on it first becoming somewhat deeper (curve *5*) but then less deep and finally disappearing (curves *6* and *7*). In 0.01 M potassium nitrate solution the minimum on the nitrate-ion wave is observed over a narrower range of lanthanum chloride concentrations ($3-5 \times 10^{-4}$ M), whereas in 1 M potassium nitrate solution such minimum is absent. Thus these phenomena are shown most clearly in 0.1 M solutions of potassium nitrate.

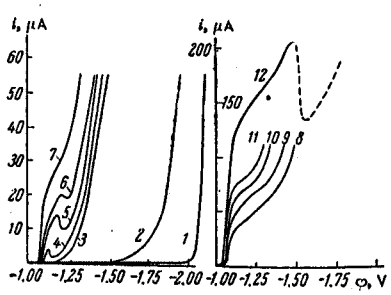

Fig. 1. Effect, on reduction of nitrate ions in 0.1 M potassium nitrate, of concentration of lanthanum chloride (M):
1) and 2) 0; 3) 2×10^{-4}; 4) 4×10^{-4}; 5) 8×10^{-4}; 6) 10^{-3}; 7) 2×10^{-3}; 8) 4×10^{-3}; 9) 6×10^{-3}; 10) 8×10^{-3}; 11) 10^{-2}; 12) 2×10^{-2}; 13) 0.1 M KCl [omitted from Figure (Ed. of Translation)].

The nitrate-ion wave has an anomalous form even in the absence of minima. Thus it occupies a very narrow potential range, only ~150 mV, and has, instead of a horizontal limiting-current plateau, only a slight inflection, this indicating some slowing down in the increase in velocity of the process with rise in cathode potential; at more negative potentials the rate of the process again increases rapidly.

The current up to the point at which it starts to fall (and in the region of the inflection on the curve when a minimum is not present) is directly proportional to the square root of the height of the mercury column h, which indicates that the rate of the process is limited at these potentials by diffusion phenomena. Since at such high concentrations the diffusion of nitrate ions cannot limit the rate of the process, the kinetics must be governed by the rate of diffusion of the lanthanum ions. This is confirmed by the fact that the current at a constant potential in the region of the inflection, for example at -1.2 V, is proportional to the $LaCl_3$ concentration (at 10^{-3} M and above — Fig. 1, curves *7–12*) raised to the power 0.83, which is close to unity. On the other hand, the current in the region of the inflection is not proportional to the concentration of nitrate ions. Thus at a lanthanum chloride concentration of 10^{-3} M the current in 0.01 M potassium nitrate is ~10 μA, in 0.1 M potassium nitrate ~25 μA, and in 1 M potassium nitrate only 50 μA. The dependence of current on nitrate concentration corresponds to a nearly linear relation between i and $\log[NO_3^-]$, which indicates that adsorption phenomena play a part in the reduction of nitrate ions. Thus the current on the nitrate-ion wave is determined on the one hand by the rate of diffusion of lanthanum ions, and on the other by the rate of the electrochemical reduction of the nitrate ions.

At a lanthanum chloride concentration of 0.02 M a deep drop in current appears afresh on the nitrate-ion wave, but at a potential of about -1.5 V (Fig. 1, curve *12*). In the vicinity of the drop in current the galvanometer readings are irregular (this part of the curve is shown broken in Fig. 1). This phenomenon is caused by the formation round the drop of a film, visible even to the naked eye, of insoluble hydrolysis products of lanthanum chloride, which retards the process. The growth and breaking off of the drop result in fissures in the film and fluctuations in the current. A certain quantity of the hydrolysis products is carried down by the mercury drops to the bottom of the cell, and prevents the drops from coalescing with the mercury which is there. On slight acidification of the solution the film dissolves, and the mercury drops coalesce. Hydrolysis ensues because the solution becomes alkaline on reduction of the nitrate ions. The second current minimum is observed only at comparatively high lanthanum chloride concentrations, which indicates that precipitation of lanthanum hydroxide is delayed at lower concentrations.

The wave due to nitrate ions in the presence of small quantities of lanthanum chloride has much in common with the previously studied[3] nitrate-ion wave in 0.1 M solutions of lanthanum chloride. Thus in both cases it begins with a sharp rise in current, which indicates that the process is autocatalytic in character. The potential ranges within which nitrate-ion waves are observed practically coincide. On acidification of the solution the start of the wave shifts to more negative potentials: *i.e.* reduction of nitrate ions becomes more difficult (Fig. 2); when the solution is made alkaline, the shift is to more negative potentials, indicating that the process is facilitated (Fig. 3). Nevertheless, it is evident from Figs. 2 and 3 that even slight acidification and addition of a little alkali lower the wave.

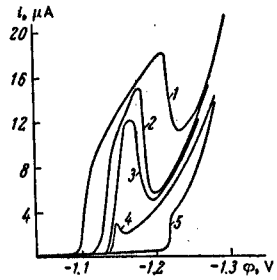

Fig. 2. Effect, on reduction of nitrate ions, of acidifying a solution of 0.1 M KNO_3 + 8 × 10^{-4} M $LaCl_3$ with hydrochloric acid to concentrations of (M): 1) 0; 2) 4 × 10^{-4}; 3) 2 × 10^{-4}; 4) 4.8 × × 10^{-4}; 5) 2.4 × 10^{-3}.

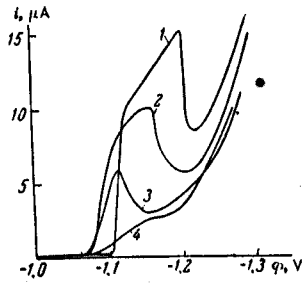

Fig. 3. Effect, on reduction of nitrate ions, of making 0.1 M KNO_3 + 7 × 10^{-4} M $LaCl_3$ solution alkaline by addition of KOH up to concentrations of (M): 1) 0; 2) 2.4 × 10^{-4}; 3) 3.9 × 10^{-4}; 4) 4.7 × × 10^{-4}.

With 0.1 M lanthanum chloride as supporting electrolyte, the wave due to 10^{-3} M potassium nitrate is also lowered when the solution is made very strongly alkaline, with a large part of the lanthanum being precipitated as the hydroxide. In both cases the lowering of the wave on addition of alkali is due to this precipitation of lanthanum. When a solution containing a low concentration of lanthanum chloride is acidified, the wave is also diminished, although this does not occur in 0.1 M solutions.

Another distinguishing feature of the nitrate-ion wave in the presence of small amounts of lanthanum chloride is the fall in the current. In the region of the minimum and at still more negative potentials the current decreases with increase in height h of the mercury column. Change in h has a similar effect under conditions corresponding to curve *3* in Fig. 1, *i.e.* at such a low concentration of lanthanum chloride that the nitrate-ion wave is not yet observed. With h unchanged and the drop time shortened artificially by means of a spatula, the current is, according to Skobets and Kavetskii[4], sharply lowered, and ultimately the wave disappears altogether. Artificial shortening of the drop time also has an appreciable effect on the nitrate wave with 0.1 M lanthanum chloride as supporting electrolyte (Fig. 4). In this case the diminution in the wave is represented by the Ilkovič equation. However, in addition to becoming smaller, the wave shifts to more negative potentials, indicating that the process slows down when the drop time is shortened.

In the presence of lanthanum salts the reduction of nitrate ions takes place autocatalytically. The process is accelerated by reaction of La^{3+} ions with OH^- ions produced on reduction of nitrate ions. It was assumed[3] that lanthanum ions favour formation of the ortho form of nitric acid. However, experiments[5] on isotopic exchange of ^{18}O between nitrate and water in the presence of a lanthanum salt did not support this view. According to a later hypothesis of Grabowski[6], partly hydrolysed lanthanum ions affect the structure of the electrical double layer on the electrode to a still greater extent than do simple hydrated lanthanum ions, and thereby accelerate the process more strongly. The disappearance of the nitrate-ion wave on acidification of the solution is due to the fact that in acid solutions the appearance of OH^- ions, which tend to make the solution alkaline on the reduction of nitrate ions, is excluded. Fig. 5 shows results for the effect of pH on the reduction of the nitrate ion with lanthanum chloride as

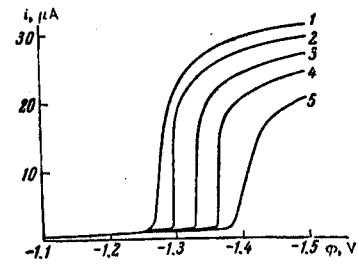

Fig. 4. Effect of drop time τ (sec) on first nitrate-ion wave in solution of 0.1 M $LaCl_3$ + + 10^{-3} M KNO_3: 1) 4.0; 2) 3.0; 3) 2.0; 4) 1.1; 5) 0.6 sec.

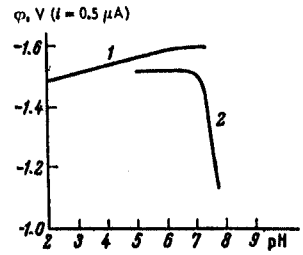

Fig. 5. Effect of pH on potential at a reduction current of the nitrate ion of 0.5 μA in 0.1 M $LaCl_3$ + 5 × 10^{-4} M KNO_3 solution: 1) acetate buffer; 2) ammonia buffer.

supporting electrolyte in acetate (curve *1*) and ammoniacal (curve *2*) buffers. The data are plotted as potential at a constant current of 0.5 μA against pH. It can be seen that in acetate solutions, instead of the expected acceleration of the process, it slows down somewhat with rise in pH. This is most probably due to complex formation by the La^{3+} ions in acetate medium, resulting in a diminished charge on the cations of the supporting electrolyte. Ammoniacal buffer solutions are characterised by a marked facilitation of the process at pH about 7, *i.e.* at the pH at which hydrolysis of lanthanum salts begins. Thus the start of the hydrolysis of a lanthanum salt is accompanied by acceleration of the reduction of nitrate ions.

The experimental results indicate that the reaction between La^{3+} and OH^- ions is slow. This follows primarily from the unusual dependence of the current on the height of the mercury column and the drop time. Such a relation between the current and the characteristics of the capillary is typical of autocatalytic processes in which the catalyst is produced slowly[7]. Examination of the structure of the electrical double layer in weakly alkaline lanthanum solutions by differential capacitance measurements[8] led to a similar conclusion. Under these conditions the capacitance of the electrode varies appreciably with time. Although the first stage in the hydrolysis of tervalent salts of the rare-earth elements, which consists essentially in simple replacement of a water molecule from the hydrated sphere of the lanthanum ion by a hydroxide ion, is rapid, subsequent stages of hydrolysis, involving the formation of soluble or colloidal polynuclear products, may occur very slowly[9]. It can therefore by assumed, as in Ref.8, that the hydrolysis products of a lanthanum salt which accelerate the reduction of NO_3^- ions are polynuclear complexes, represented, for example, by the general formula $La_x(OH)_y^{(3x-y)+}$ and carrying a high positive net charge.

Two alternative explanations can be put forward for the appearance of a drop in the current on the nitrate-ion wave in the presence of small quantities of lanthanum chloride. The first explanation is based on the dependence of the ψ'-potential on the electrode potential. With increase in the negative electrode potential the positive ψ'-potential decreases, passes through zero at the zero-charge point, and assumes increasing negative values. The reduction of anions begins to be inhibited owing to electrostatic repulsion, and a fall in current appears on the polarisation curve, as in the case of the reduction of persulphate ions. In the presence of polynuclear cations adsorbed in more than equivalent amount, the transition of the ψ'-potential to negative values should occur at considerably more negative potentials than the zero-charge point. According to this explanation, polarisation curves obtained in this work are analogous to reduction curves of persulphate ions in the presence of small quantities of lanthanum ions[10]. The difference is merely that, in the reduction of persulphate ions unaccompanied by the appearance of hydroxide ions, the reaction is accelerated by simple hydrated La^{3+} ions, not by a hydrolysis product thereof.

The second explanation is that, with increase in cathode potential, the conditions of adsorption of polynuclear complex lanthanum ions change, which may result in a change in sign of the ψ'-potential or a decrease in its positive magnitude. With such an interpretation the minima on the nitrate and persulphate waves would have different causes, in spite of their apparent similarity, since in the reduction of nitrate ions the drop in current would be due to a decrease in catalyst concentration in the surface layer at a sufficiently negative potential, whereas in the reduction of persulphate ions the minimum is caused by a drop in concentration of the depolariser at the electrode surface under the same conditions.

Available experimental data are insufficient for a final choice of explanation, although they are probably more consistent with the second theory. According to them the composition of the solution has a substantial effect on the kinetics of the reduction of nitrate ions, probably owing to a change in the conditions of adsorption of catalytically active species on mercury. It is apparently for this reason that the polarisation curves of lithium nitrate in the presence of small quantities of lanthanum chloride (Fig. 6) have a somewhat different form. On these curves the minimum is hardly noticeable. Consequently, replacement of K^+ by Li^+ ions has an appreciable effect on the reduction of nitrate ions. Replacement of K^+ by Cs^+ ions has practically no effect. Addition of lithium chloride to lithium nitrate solution containing 10^{-3} M lanthanum chloride results in the development of a large maximum (Fig.7), which is not polarographic in character; with a high total concentration of lithium ions the reduction wave of nitrate ions disappears. The wave simply disappears on addition of potassium chloride to lithium nitrate solution, and also

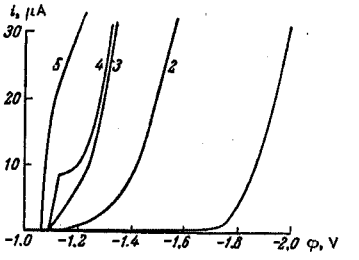

Fig. 6. Effect, on reduction of nitrate ions in 0.1 M lithium nitrate, of lanthanum chloride concentration (M):
1) 0; 2) 10^{-4}; 3) 8×10^{-4}; 4) 10^{-3}; 5) 2×10^{-3}.

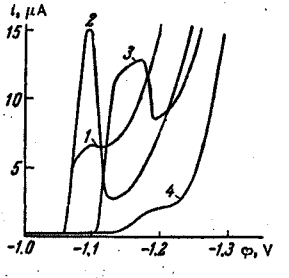

Fig. 7. Effect, on nitrate-ion wave in 0.1 M $LiNO_3 + 10^{-3}$ M $LaCl_3$ solution, of concentration of added lithium chloride (M): 1) 0; 2) 0.3; 3) 0.5; 4) 0.7.

on addition of caesium chloride to lithium nitrate solution, and of strontium chloride to potassium nitrate solution†. Increase in concentration of cations from the supporting electrolyte is known to make the ψ'-potential more positive, which should accelerate the reduction of anions. The observed retardation of the process should therefore be attributed to a change in adsorption of catalyst species.

Addition of gelatin results in a diminution in the reduction currents due to the nitrate ions, then to complete disappearance of the wave (Fig. 8). Small quantities of hexyl alcohol exert only an inhibiting action (Fig. 9, curve *2*), but at higher concentration the negative shift in the wave is accompanied by a growth in current in the region of the minimum until the latter completely vanishes (curves *3–5*).

Quite often surface-active substances are found to affect the electrode process differently at different concentrations. For example, such effects are observed in the electrochemical reduction of other anions. Thus it follows from

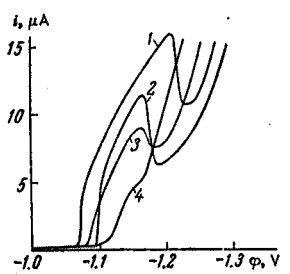

Fig. 8. Effect, on nitrate-ion wave in 0.1 M KNO_3 + 7×10^{-4} M $LaCl_3$ solution, of concentration of added gelatin (%): 1) 0; 2) 0.0012; 3) 0.0028; 4) 0.004.

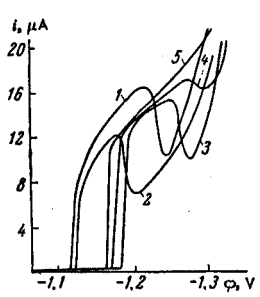

Fig. 9. Effect, on nitrate-ion wave in 0.1 M KNO_3 + 7×10^{-4} M $LaCl_3$ solution, of concentration of added hexyl alcohol (M): 1) 0; 2) 1.47×10^{-2}; 3) 4.03×10^{-2}; 4) 5×10^{-2}; 5) 5.63×10^{-2}.

† These results are tentative.

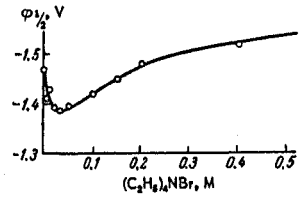

Fig. 10. Effect of concentration of tetraethylammonium bromide as supporting electrolyte on the half-wave potential of 10^{-3} M potassium iodate.

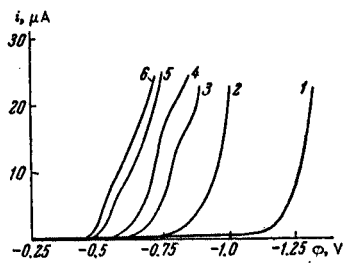

Fig. 11. Effect, on reduction of bromate ions in 0.1 M potassium bromate, of concentration of lanthanum chloride (M): 1) 0; 2) 8×10^{-5}; 3) 2×10^{-4}; 4) 4×10^{-4}; 5) 6×10^{-4}; 6) 10^{-3}.

Fig. 10 that, with increasing concentration of tetraethylammonium bromide used as supporting electrolyte, the reduction of iodate ions is first accelerated and then retarded. In this case the accelerating effect is probably caused by a shift in the ψ'-potential to more positive values, while retardation at higher concentrations is due to blocking of the cathode surface by the tetraethylammonium cations (see also Ref. 11). Reduction of bromate ions in the presence of small amounts of lanthanum chloride (Fig. 11) takes place in a different range of potentials. Therefore a minimum is not observed on the polarisation curves, although in other respects addition of lanthanum chloride affects the reduction of bromate ions similarly to that of nitrate ions.

In view of the above data indicating the strong catalytic action of lanthanum ions on the reduction of anions at a dropping mercury electrode, an attempt was made to obtain the reduction wave of chlorate ions at high concentrations in the presence of small quantities of lanthanum chloride. Direct electrochemical reduction of the chlorate ion was not observed under other conditions. It was found, however, that reduction of the chlorate ion does not occur even under the conditions of our experiment.

The writers would like to express their gratitude to Academician A. N. Frumkin for valuable comments in discussing the results.

SUMMARY

1. A study has been made of the reduction of nitrate ions at a dropping mercury electrode in the presence of small quantities of lanthanum ions. Under these conditions reduction takes place autocatalytically, formation of the catalyst by reaction of La^{3+} ions with OH^- ions taking place slowly.
2. The adsorbability on mercury of catalytically active polynuclear hydroxo-ions of lanthanum depends on the electrode potential and the composition of the solution.

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INDICATION OF CHEMICAL INTERACTION ON VISCOSITY ISOTHERMS IN BINARY SYSTEMS

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The existing classification of viscosity diagrams of binary systems[1] assumes that there is no chemical interaction in systems in which the viscosity isotherms are convex to the composition axis. However, the literature reports a considerable number of binary systems in which the components undoubtedly interact, whose viscosity isotherms are nonetheless convex with respect to the composition axis. The occurrence of interaction in the liquid phase in these systems is demonstrated either by other methods of physicochemical analysis or is confirmed by the evolution of a large amount of heat on mixing or by a change in colour. This finding casts doubt on the use of isotherms convex to the composition axis as criteria of compound formation.

Experimental results on the viscosity of systems in which a reaction of the type A + B = AB takes place leave no doubt that this type of reaction results in an increase in viscosity. In view of this the occurrence of such convex isotherms in systems showing interaction is explained by the fact that the amount of compound AB formed is insufficient to lead to the appearance of a maximum or to an isotherm which is monotonically concave to the composition axis (at no point does $d\eta/dx = 0$). Nevertheless, this interaction should result in positive deviations from the viscosity isotherm calculated on the assumption that there is no interaction. My proposed method[2] of calculating the viscosity isotherm in binary systems with non-interacting components enables the magnitude of these deviations to be computed, and in most cases the composition of the resulting compound to be determined from the location of the maximum deviation in the viscosity from the calculated value. Below are given several examples of this type of analysis, based on reliable data on viscosity isotherms taken from the literature.

Pentachloroethane–Acetone System

When this system was first investigated at 25°, Sakhanov and Ryakhovskii[3] pointed out the inconsistency between the shape of the viscosity isotherm, convex to the composition axis (see accompanying diagram), and the considerable amount of heat evolved and great contraction observed when the components were mixed. In their opinion these last two facts indicate chemical interaction between pentachloro: ethane and acetone. It may be added that the presence of chemical interaction has been established, and studied in detail on the basis of many properties, in the analogous system chloroform–acetone[4]. Reaction between pentachloroethane and acetone is clearly reflected on the $\Delta\eta$–composition diagram [$\Delta\eta$ here denotes the difference between experimental viscosity values (curve *1*) and the viscosity isotherm calculated on the assumption that interaction is absent (curve *2*)]. From Table 1 and the diagram (curve *3*) it can be seen that maximum values of $\Delta\eta$ occur at a molar ratio of the components of 1 : 1.

Diphenylamine–Acid Systems

Udovenko and Topornina[5] made a viscosity study of the systems formed by diphenylamine with acetic and hexanoic acids. Diphenylamine is known to exhibit very feebly basic

TABLE 1. Deviations in viscosity from values calculated on the assumption of the absence of interaction ($\Delta\eta$ values) for the pentachloroethane–acetone system at 25°.

Acetone, mole %	$\Delta\eta$, cP
30	0.070
40	0.098
45	0.112
47	0.117
50	0.122
52	0.120
55	0.114
60	0.104