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Stabilisation of the Surface Potential and Determination of the Activities of Individual Ions in Solution

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The problem of the determination of the thermodynamic characteristics of individual ions, the Galvani potentials, and the liquid junction potentials by a method based on the stabilisation of the surface potentials of electrolyte solutions is examined. The results of experiments on the applications of surface-active agents (aliphatic carboxylic acids, alcohols and amines) as stabilisers of the surface potentials are discussed. The scope and limitations of the method are indicated. The bibliography includes 85 references.

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I. INTRODUCTION

The problem of determining the thermodynamic characteristics of individual ions and their variation with the composition of the medium still remains controversial in the physical chemistry of electrolyte solutions. The development of ideas in this field has been notably influenced by Guggenheim [1,2], who formulated the following principle: "the electrical potential difference between two points in different media can never be measured and has not yet been defined in terms of physical realities. It is therefore a conception which has no physical significance"[2]. From this point of view, the Galvani potential between the electrode and the electrolyte solution, the liquid junction potential (diffusion potential), and the potential difference between the gas phase (or vacuum) and a condensed phase (the surface or χ-potential) are not susceptible to experimental determination and lack physical significance. The above potential differences are functionally related to the activities and other thermodynamic characteristics of individual ions in solution (see, for example, Izmailov [3]). Thus the latter cannot be measured either and lack physical significance. Furthermore, according to Guggenheim there is no need for their determination, since the thermodynamic state of an electrolyte solution can be described in terms of the thermodynamic characteristics of the electrolyte as a whole or electrically neutral combinations of the charged components of the solution, which are susceptible to experimental determination.

Up to the present time, the majority of investigators have not shared Guggenheim's radical view, although the thesis that the thermodynamic characteristics of individual ions are not susceptible to the determination within the framework of rigorous thermodynamics appears to be generally accepted. The possibility, in principle, of measuring the potentials of individual electrodes was demonstrated in recent studies [4,5], although it has still not proved possible to develop experimental methods based on these ideas. The greatest progress has been achieved in the development of methods for the estimation of the thermodynamic characteristics of individual ions based on

different kinds of non-thermodynamic assumptions. The results obtained by these methods are discussed in a number of monographs [3,6,7] and reviews [8-10]. The available methods based on non-thermodynamic assumptions have been classified in the review by Popovych [8], who divides them into two categories. The first includes methods based on the estimation of the liquid junction potentials (Bjerrum and Larsson [11], Oiwa [12] and Parker and coworkers [13]) and the second includes methods involving correlations between the dimensions of ions and molecules and their solvation energies (Pleskov's normal cell method [14], Strehlow's ferrocene–ferricinium electrode method [15], Izmailov's extrapolation methods [16,17], Grunwald's standard electrolyte method [18], de Ligny's method [19], and others). Furthermore, Popovych considers in a separate category methods based on the estimation of Galvani potentials. The usefulness of these methods for the solution of the problem under discussion has been frequently noted [20]. This review deals with the problem of using the method based on the stabilisation of the χ-potentials of electrolyte solutions for the estimation of the activities of individual ions and the solvent effects for such ions and also to determine the Galvani potentials and liquid junction potentials.

II. PRINCIPLES OF THE SURFACE POTENTIAL STABILISATION METHOD

1. Calculation of the Thermodynamic Characteristics of Individual Ions from the Real Potentials of Ions and the Surface Potentials of Solvents

The principle of the calculation of the thermodynamic characteristics of individual ions in solution using the χ-potentials of the solvent was formulated after the development of the concept of the real potential† (real solvation energy) of ions α_i (Frumkin [22], Lange and Mishchenko [23]). According to Lange and Mishchenko [23], the real potential of ions α_i is related to their chemical potential (chemical solvation energy) μ_i as follows:

$$\alpha_i = \mu_i + z_i F \chi, \tag{1}$$

where z_i is the ionic charge and F the Faraday. The potentials α_i can be calculated directly from experimental data [24-27]. For ions in aqueous solutions, the most reliable data have been obtained by Randles [27], who estimates the error in the α_i for cations as ±0.5 kcal g-ion^{-1} and for anions as ±1 kcal g-ion^{-1}. The χ-potentials of solvents, which are defined as potential differences between points in different media, are inaccessible to direct measurements. Theoretical calculation of this quantity for water leads to an improbably high result [28]. Estimates of χ_{H_2O} based on non-thermodynamic assumptions have been frequently made [25,26,29-34]. The values of χ_{H_2O} obtained vary from −0.5 to 1.0 V. The low accuracy of the α_i and the uncertainty in χ for water and other solvents vitiate at present the attempts to obtain accurate values of $\lg \gamma_i^\circ$ (the so-called medium effects) or other corresponding thermodynamic characteristics of individual ions in terms of the absolute values of α_i.

†In defining the concepts of the electrochemical, real, and chemical potentials of ions, we follow the terminology employed by Parsons [21].

2. Non-thermodynamic Assumption of a Constant Surface Potential

It is easier to estimate the medium effects and the activities of individual ions in terms of the changes in the real and χ-potentials. Eqn. (1) can be transformed as follows:

$$\Delta\alpha_i = \Delta\mu_i + z_i F \Delta\chi, \tag{2}$$

where $\Delta\alpha_i$ is the change in the real potential of the ith ion and $\Delta\chi$ the change in surface potential on passing from one solution to another. It follows from Eqn. (2) that, when the surface potentials of solutions are stabilised (i.e. when $\Delta\chi = 0$), the values of $\Delta\alpha_i$ determined experimentally are equal to the corresponding changes in the chemical potential of ions of type i. Measurements of $\Delta\alpha_i$ on passing from one solvent to another have recently become common [36-41]. The experimental determination of $\Delta\alpha_i$ is based on the following factors. The real potential α_i is related to the electrochemical potential $\bar{\mu}_i$ by the familiar expression

$$\bar{\mu}_i = \alpha_i + z_i F \psi, \tag{3}$$

where ψ is the external potential of the phase. If two conducting phases whose interface is permeable only to charged species of type i are brought into electrical contact, the electrochemical potentials of such species in these phases become equal:

$$\bar{\mu}_i^{(1)} = \bar{\mu}_i^{(2)} \ . \tag{4}$$

Using Eqn. (3), one can write

$$\alpha_i^{(1)} + z_i F \psi^{(1)} = \alpha_i^{(2)} + z_i F \psi^{(2)}, \tag{5}$$

or

$$\Delta\psi = \psi^{(1)} - \psi^{(2)} = (\alpha_i^{(2)} - \alpha_i^{(1)})/z_i F = \Delta\alpha_i/z_i F, \tag{6}$$

where $\Delta\psi$ is the difference between the external potentials or the Volta potential difference arising between phases (1) and (2) as a result of the contact between them. Rabinovich [42] showed that more correctly the potential $\Delta\epsilon$, compensating $\Delta\psi$, is proportional to $\Delta\alpha_i$, rather than $\Delta\psi$ itself, since at the instant of compensation the phases are subjected to the same potential relative to earth and therefore there is no need for the assumption that the real potential is independent of the charge of the phase (Bridgman's hypothesis [43]). Henceforth, we shall call $\Delta\epsilon$ the "compensating potential"‡. Consequently, one can write

$$\Delta\varepsilon = \Delta\alpha_i/z_i F. \tag{7}$$

The interfaces between electrolyte solutions are permeable to both cations and anions. Nevertheless, systems permeable to ions of only one type can be produced by means of reversible ion-selective electrodes. We shall consider the specific instance of solutions of a strong acid HA for which it is necessary to determine the thermodynamic state of H^+ ions. Isolated HA solutions in which two reversible hydrogen electrodes are immersed and which are joined by a metallic conductor constitute a system permeable to H^+ ions only (Fig. 1*a*). One of the HA solutions will be regarded as the standard and the

‡The condenser and ionisation methods as well as flow methods are equally suitable for the measurement of $\Delta\epsilon$. Kenrick's method [44] has been widely used hitherto for the determination of $\Delta\alpha_i$. The technique of the measurements has been described in detail [45].

other as the test solution. As a result of contacts via the hydrogen electrodes, the previously electrically neutral HA solutions are charged relative to one another and a Volta potential difference arises between their free surfaces. The contact charging of solution is due to the fact that, by virtue of the difference between their compositions, the electrochemical potentials of the H^+ ions in them are different too. By virtue of the equilibrium $H^+ + e \rightleftharpoons \frac{1}{2}H_2$ between the solution and the electrodes, the electrochemical potentials $\bar{\mu}_e$ of the electrons in the solid phase of the electrodes should also be different. Contact between the hydrogen electrodes leads to the equalisation of the $\bar{\mu}_e$, which shifts the equilibrium $H^+ + e \rightleftharpoons \frac{1}{2}H_2$. As a result, a number of H^+ ions disappear from the HA solution where their activity is higher and an equal number appear in the solution where their activity is lower. The compensating potential $\Delta\epsilon$ which shifts the equilibrium in the system so that the Volta potential difference $\Delta\psi$ between the solutions becomes zero can be selected by means of a potentiometer included in the circuit between the hydrogen electrodes (Fig. 1*b*). For the given specific case, Eqn. (7) becomes

$$\Delta\varepsilon = [\alpha_{H^+}(m) - \alpha_{H^+}(m_{st})]/F, \qquad (8)$$

where $\alpha_{H^+}(m)$ and $\alpha_{H^+}(m_{st})$ are the real potentials of H^+ ions in the test and standard solutions respectively. The electrochemical system illustrated in Fig. 1*a* is usually represented symbolically as follows:

$$Pt(H_2)\,|\,HA,\ m_2\,|\,air\,|\,HA,\ m_{st}\,|\,Pt(H_2). \qquad (A)$$

In contrast to the usual galvanic cells, such systems will be called Voltaic cells.

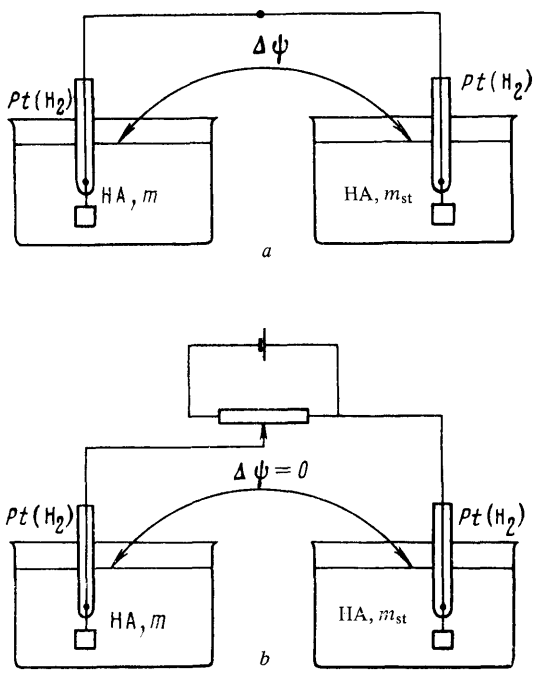


Figure 1. Schematic illustration of the electrochemical system used to investigate the Volta effect on joining together two electrolyte solutions via ion-selective electrodes: *a*) contact charging of the solutions; *b*) compensation of the Volta potential difference produced using a potentiometer to generate a compensating potential.

According to Eqns. (2) and (7), the compensating potential of the voltaic cell (A) is proportional to the difference between the chemical potentials of H^+ ions in the test and standard solutions when the difference between the potentials jumps at the interfaces *2* and *3* in the cell is zero ($\Delta\chi = 0$). This condition holds when the solutions being compared are fairly dilute or when their surface potentials are artificially stabilised. With the aid of the voltaic cell (A), it is in essence possible to determine $\mu_{H^+} - \mu^\circ_{H^+}$ to within the unknown value of $F\Delta\chi$.

The assumption that $F\Delta\chi$ is zero implies the non-thermodynamic assumption of the equality of the surface potentials of the solutions being compared. In practice, it is more convenient to employ, instead of a voltaic cell of type (A), a voltaic cell of the following type:

$$Pt(H_2)\,|\,HA,\ m\,|\,air\,|\,standard\ solution\,|\,reference\ electrode, \qquad (A')$$

the $\Delta\epsilon$ values for which can be readily converted into the $\Delta\epsilon$ value for a cell of type (A) by a computational procedure.

On the basis of the non-thermodynamic assumption of equal surface potentials, a voltaic cell of type (A) essentially permits an experimental determination of the dependence of the Galvani potentials of the individual electrodes on the composition of the electrolyte solution. A similar relation for the liquid junction potentials permits a determination for voltaic cells of the type

$$Hg\,|\,Hg_2Cl_2\,|\,saturated\ KCl\ solution\,|\,HA,\ m\,|\,air\,|\,standard\ solution\,|\ reference\ electrode. \qquad (B)$$

Indeed if the potential jump at the interface between the HA solution and air does not vary with the composition of the solution, the change $\Delta\epsilon$ for a voltaic cell of type (B) is due exclusively to the change in the liquid junction potential ΔE_j at the interface between the HA solution and the saturated KCl solution.

3. The Concepts of the "Real" Ionic Activity and the "Real" Acidity of the Medium

For further exposition, it is important to consider the concepts of the "real" ionic acitivity in solution [46] and the "real" acidity of the medium [47]. The activities of individual ions in solution a_i as well as the activities of the electrically neutral components are usually defined by the equation

$$\mu_i = \mu_i^\circ + RT\ln a_i = \mu_i^\circ + RT\ln m_i\gamma_i, \qquad (9)$$

where μ_i° is the chemical potential of ions of type i in the standard state, γ_i their chemical activity coefficient in the test solution, and m_i their molality. However, a physical interpretation of Eqn. (9) is difficult, because it is impossible to imagine a real transfer of the charged solution component from the standard state to the test solution without crossing the interface. Rabinovich et al. [46] suggested that the thermodynamic activities of ions in solution be defined by the equation

$$\alpha_i = \alpha_i^\circ + RT\ln a_i^r = \alpha_i^\circ + RT\ln m_i\gamma_i^r, \qquad (10)$$

where m_i, a_i^r, and γ_i^r are the molality, real activity, and real activity coefficient of species of type i respectively. In the special case of H^+ ions the quantity $-\ln a^r_{H^+} = pa^r_H$ will be called the real acidity of the solution (medium). The following real physical process corresponds to Eqn. (10): the transfer of one gramme-ion of charged species of type i from the electrically neutral test phase to the standard phase (Fig. 2). The ions pass from the test

phase to a point in the gas phase (or *in vacuo*) at an infinite distance from the test phase, crossing the boundary between the test phase and air; in this process they overcome the energy barrier due to the electrical double layer at this boundary, which is characterised by the χ-potential of the phase. In such a transition it is necessary to expend work equal to the real solvation energy of species of types i in the test phase. Next the ions pass from the gas phase to the standard phase, also crossing (this time in the opposite direction) the corresponding interface. This transition involves a gain in work equal to the real solvation energy of species of type i in the standard phase. Thus the quantities a_i^r and γ_i^r are measures of the change in the real solvation energy (real potential) of the charged species on passing from the standard state to the test solution. If the transfer process proceeds under the conditions of equal surface potentials of the phases ($\Delta\chi = 0$), then, according to Eqns. (2) and (9), the real activity and activity coefficient are equal to the corresponding chemical quantities.

We shall employ the same formal treatment for the real activities and activity coefficients of ions as for the mean ionic activities and activity coefficients of electrolytes. The overall real activity coefficient γ_i^r becomes unity only at infinite dilution in aqueous solution. For the test solvent, γ_i^r tends to a limiting value $\gamma_i^{r\circ}$ when $m_i \to 0$. We shall call this value the real solvent activity coefficient. The activity coefficients γ_i^r and $\gamma_i^{r\circ}$ are linked by the relation

$$\gamma_i^r = \gamma_i^{r*}\gamma_i^{r\circ}. \qquad (11)$$

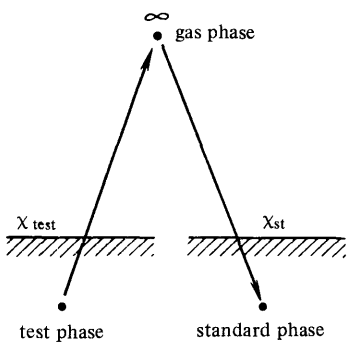


Figure 2. Schematic illustration of the transfer of the charged component of the electrolyte solution from the test phase to the standard phase via the gas phase.

The coefficient γ_i^{r*}, which we shall call the real concentration activity coefficient, becomes unity at infinite dilution in the given solvent. Finally, the product of the real activity coefficients of the electrolyte ions is equal to the square of the mean ionic activity coefficient:

$$\gamma_+^r\gamma_-^r = \gamma_\pm^2. \qquad (12)$$

The activity coefficients $\gamma_\pm$, $\gamma_\pm^*$, and $\gamma_\pm^\circ$ are usually called the overall, salt, and solvent effects of the medium respectively. However, this terminology is inapplicable to real activity coefficients, since their numerical values, obtained from experimental data, depend not only on the state of the ions in the bulk of the solution but also on the electrical states of the surfaces of the solutions being compared. Only when the experiment is carried out under the conditions of equal χ-potentials of the solutions being compared can the real activity coefficients be interpreted as medium effects for the individual ions.

III. DISCUSSION OF EXPERIMENTAL RESULTS OBTAINED BY THE SURFACE POTENTIAL STABILISATION METHOD

The stabilisation of the χ-potential by surface-active substances was observed[48] for HCl solutions. The authors determined the real activity coefficients of H^+ and Cl^- ions in aqueous and aqueous alcoholic HCl solutions by measuring the compensating potentials of the voltaic cell

$$Ag \mid AgCl \mid HCl, m \mid air \mid KCl, m_{st} \mid AgCl \mid Ag,$$

and the electrical potentials of the galvanic cells

$$Pt(H_2) \mid HCl, m \mid AgCl \mid Ag.$$

It was found that the values of $\gamma_{H^+}^{r*}$ and $\gamma_{Cl^-}^{r*}$, which differ sharply from one another and from the $\gamma_\pm^*$ in pure HCl solutions, approach one another and almost coincide with the $\gamma_\pm^*$ for solutions to which 1% of n-pentyl alcohol has been added (Table 1). This was given the following explanation, which subsequent studies showed to be inaccurate. Molecules of n-pentyl alcohol, which have a higher adsorption potential at the solution–air interface, displace the ions and undissociated HCl molecules from the surface layer of the solution, as a result of which the electrical properties of the surfaces of the HCl solutions become the same for different compositions.

Table 1. The real activity coefficients of H^+ and Cl^- ions in pure aqueous HCl solutions (*a*) and in HCl solutions containing 1% of n-pentyl alcohol (*b*) at 25°C.

HCl, M	*a*		*b*		*a*
	$\gamma_{H^+}^{r*}$	$\gamma_{Cl^-}^{r*}$	$\gamma_{H^+}^{r*}$	$\gamma_{Cl^-}^{r*}$	$\gamma_\pm^*$
0.01	0.82	0.99	0.90	0.94	0.90
0.02	0.79	0.98	0.87	0.92	0.88
0.05	0.74	0.94	0.82	0.88	0.83
0.10	0.70	0.89	0.78	0.86	0.80
0.20	0.71	0.82	0.73	0.85	0.77
0.50	0.98	0.59	0.72	0.85	0.76

The observed stabilisation of the χ-potentials of aqueous HCl solutions was then used[49] to determine the acidity of the medium in the HCl–H_2O system over the complete range of compositions. Voltaic cells of type (A′) were used for the measurements. The HCl–H_2O mixtures investigated were saturated with surface-active alcohols and aliphatic acids. The authors observed that the experimental real acidities pa_H^r of the solutions stabilised by heptyl and nonyl alcohols agreed with the corresponding Hammett acidity functions H_0,[50] while the pa_H^r for pure HCl solutions differed sharply from the H_0 (Table 2). Table 2 shows that significant discrepancies between pa_H^r and H_0 for solutions with heptyl alcohol are observed for concentrations of 12 M and above and for solutions saturated with n-nonyl alcohol for concentrations of 14 M and above. The mutual approach of the

values of pa_H^r and H_0 was explained by the complete equalisation of the χ-potentials of the HCl solutions when the latter were saturated with a surface-active agent, whose molecules displaced the electrolyte (HCl) from the surface layer. The agreement between the acidities of the medium obtained by fundamentally different methods is itself remarkable if one recalls that more than 10 different indicator acidity scales[51] are known at present for the H_2SO_4–H_2O, $HClO_4$–H_2O, and HCl–H_2O systems, which do not agree. This provides some justification for the interpretation of both the pa_H^r and H_0 values for HCl solutions as the protic activities of the medium pa_H.

Table 2. Comparison of the acidity functions for HCl–H_2O solutions on the basis of the results of Rybkin and Shevchenko[49].

Molality of HCl	pa_H^r			$-H_0^*$ (pure HCl soln.)
	pure HCl soln.	HCl soln. satd. with n-heptyl alcohol	HCl soln. satd. with n-nonyl alcohol	
0.5	−0.25	−0.26	−0.30	−0.28
1.0	0.36	0.13	0.11	0.07
2.0	1.30	0.50	0.50	0.50
3.0	2.16	0.81	0.81	0.83
4.0	2.96	1.12	1.14	1.15
5.0	3.73	1.47	1.47	1.48
6.0	4.45	1.75	1.75	1.77
7.0	5.23	2.06	2.03	2.06
8.0	6.05	2.35	2.34	2.36
10.0	7.37	2.92	2.89	2.88
12.0	8.75	3.50	3.40	3.37
14.0	9.90	4.16	4.01	3.86
16.0	10.91	4.85	4.65	4.35

*According to the results of Vinnik et al.[50]

The study of the stabilisation of the χ-potentials of solutions of strong inorganic acids was continued in another investigation[52], where the χ-potential shifts for the HCl solutions at different concentrations under the influence of surface-active alcohols were determined with the aid of a voltaic cell of type (B). Figs. 3 and 4 and Table 3 illustrate the results of this study in relation to the χ-potential shifts due to the adsorption of n-heptyl and n-perfluoroheptyl alcohols. Whereas the χ-potential shift on passing from pure 0.1 M HCl solution to the corresponding HCl solution saturated with n-heptyl alcohol is about 300 mV, the shift for the 15 M HCl solution is about 550 mV.

This was explained[52] by the fact that in concentrated HCl solutions the formation of a monolayer of the surface-active alcohol at the solution–air interface is accompanied by the disruption of the double layer due to the adsorption of HCl. Another explanation is also possible. The monolayer of the surface-active molecules screens the adsorption layer formed by the HCl dipoles, as a result of which the latter does not influence the external potential of the solution. Therefore, when HCl solutions are saturated with a surface-active alcohol, their χ-potentials are determined only by the monolayer of the surface-active molecules, regardless of the HCl concentration, and are therefore the same for all HCl solutions. Since the adsorption of n-heptyl alcohol and of HCl shift the χ-potential of water in opposite directions, these effects are combined and the overall shift of the χ-potentials of concentrated HCl solutions is large.

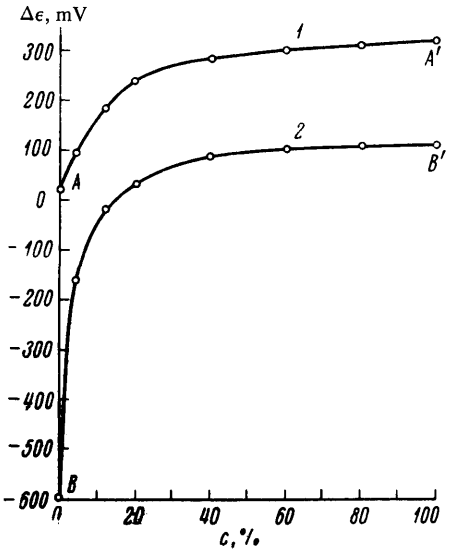


Figure 3. The adsorption shift of the χ-potentials of HCl solutions following their saturation with n-heptyl alcohol [1) 0.32 M HCl; 2) 16.42 M HCl]. The concentration c of the surface-active agent, expressed as a percentage relative to its concentration in the saturated solution, is plotted as abscissa.

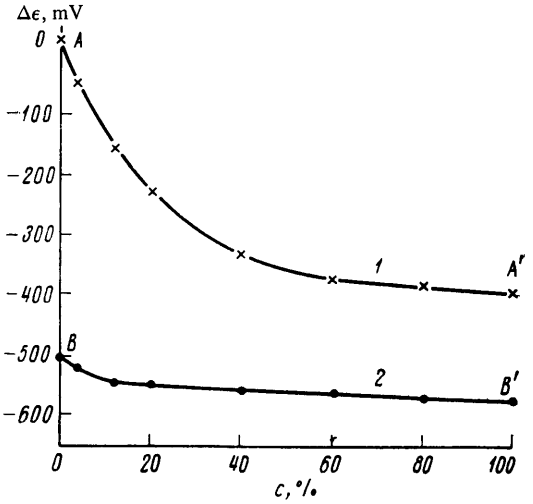


Figure 4. Adsorption shift of the χ-potentials of HCl solutions following their saturation with n-perfluoroheptyl alcohol [1) 0.3 M HCl; 2) 14.7 M HCl]. The concentration c of the surface-active agent, expressed as a percentage relative to its concentration in the saturated solution, is plotted as abscissa.

In conformity with the foregoing considerations, the lengths of the $A'B'$ sections in Figs. 3 and 4 can be interpreted as representing the change in the compensating potential of a cell of type (B) caused exclusively by the change in the liquid junction potential ΔE_j at the interfaces between the test solutions and the saturated KCl

solution as the HCl concentration is varied. The lengths of the *AB* sections in these figures reflect the changes in $\Delta\epsilon$ for a cell of type (B) caused both by the shift of the χ-potential of water following the adsorption of HCl at the solution–air interface and by ΔE_j as the HCl concentration is varied. If it is assumed that the ΔE_j are independent of the presence of the surface-active agent in the HCl solutions, it is easy to calculate the change in the adsorption potential of hydrochloric acid ΔE_{HCl} at the solution–air interface with change in the HCl concentration. The adsorption potential of HCl (ΔE_{HCl}) is understood as the component of $\Delta\epsilon$ for a voltaic cell of type (B) due to the adsorption of HCl alone at the solution–air interface. The numerical values of ΔE_{HCl} are equal to the lengths of the *AB* and *A'B'* sections and are listed in Table 3.

Table 3. The acidity functions pa_H^r and H_0, the HCl adsorption potentials, the liquid junction potentials in cell (B), and the compensating potentials in cell (B) for aqueous HCl solutions at 25°C.

HCl, mole %	$-pa_H^r$		$-H_0$	ΔE_{HA}^{**}, mV	ΔE_j*, mV	ΔE***, mV
	pure solns.	stabilised solns.*				
1	—0.10	—0.14	—0.13	12	2	14
2	0.52	0.24	0.27	22	6	28
3	1.08	0.49	0.51	35	10	45
4	1.56	0.71	0.74	50	16	66
5	2.00	0.92	0.96	64	23	87
6	2.55	1.14	1.16	83	28	111
7	3.08	1.36	1.36	102	35	137
8	3.60	1.58	1.57	119	45	164
9	4.13	1.80	1.76	138	53	191
10	4.60	2.01	1.94	153	67	220
12	5.74	2.44	2.20	195	82	277
14	6.83	2.85	2.68	235	95	330
16	7.90	3.24	3.07	276	114	390
18	8.90	3.62	3.44	312	141	453
20	9.83	3.98	3.80	346	169	515
22	10.73	4.30	4.14	380	197	577

*Averaged for solns. stabilised with n-heptyl, n-perfluoroheptyl and isopentyl alcohols.

**The positive sign ΔE_j, ΔE_{HA}, and $\Delta\epsilon$ implies that the reference electrode in a cell of type (B), immersed in the standard solution, becomes more positive owing to these potential shifts relative to the calomel electrode in the test solution.

***Referred to the compensating potential of a cell of type (B) for pure 0.01 M HCl solution.

The curves in Fig. 4 represent the χ-potential shifts for HCl solutions under the influence of n-perfluoroheptyl alcohol, which displaces the potential of water in the same direction as that of HCl. Therefore, the overall shift of the χ-potential diminishes with increase of HCl concentration and it may happen that in concentrated HCl solutions the surface activity of n-perfluoroheptyl alcohol is reduced. It is interesting that, when n-heptyl and n-perfluoroheptyl alcohols are used, similar values of ΔE_j and ΔE_{HCl} are obtained. Figs. 3 and 4 also show that the "tail" sections of the curves relating $\Delta\epsilon$ to the concentration of the surface-active agent are almost parallel.

When the variation of ΔE_{HCl} with the concentration of the surface-active agent is determined, it is found that, at a relative concentration of n-heptyl alcohol of 4%, the adsorption potential ΔE_{HCl} is already close to zero.

Thus, at comparatively low concentrations of the surface-active agent, the electrical properties of the surfaces of the solutions already approach those of the surface of the solution saturated with the surface-active alcohol. As before[49], the values of pa_H^r found from the observed ΔE_j and the experimental data for the cells with transport

$$Pt(H_2)\,|\,HCl,\ m\,|\,\text{sat. KCl soln.}\,|\,\text{reference electrode}\ \S$$

proved to be extremely close to the corresponding acidity functions H_0.[53]

The results of experiments on the stabilisation of the χ-potentials of concentrated HBr and $HClO_4$ solutions have been published[54]. Calculation of pa_H^r for HBr solutions from experimental data for cells of types (B) and (B') on the assumption that the surface-active agent (n-heptyl alcohol) causes the complete equalisation of the χ-potentials of the HBr solutions leads to values which differ appreciably from the corresponding acidity functions H_0 [55] (Table 4). This result can be explained by the fact that n-heptyl alcohol only partially stabilises the χ-potentials of HBr solutions. The monolayer of n-heptyl alcohol molecules, screening the adsorption layer of HBr dipoles, cannot constitute an obstacle to the electrostatic field generated by the Br^- ions which have undergone specific adsorption at the solution–air interface.

Table 4. The acidity functions pa_H^r and H_0, the adsorption potentials ΔE_{HA} and ΔE_{A^-}, the changes in the liquid junction potential ΔE_j in cell (B), and the compensating potentials $\Delta\epsilon$ in cell (B) for $HBr–H_2O$ solutions at 25°C.

HBr, mole %	$-pa_H^r$			$-H_0$	ΔE_{HA}, mV	ΔE_{A^-}, mV	ΔE_j, mV	$\Delta\epsilon$, mV
	pure solns.	solns. satd. with surface-active agent	with allowance for ΔE_{A^-}					
1	—0.09	—0.22	—0.32	—0.32	8	5	5	18
2	0.66	0.32	0.18	0.15	20	9	8	37
3	1.25	0.69	0.46	0.42	33	13	15	61
4	1.81	1.03	0.72	0.67	46	18	21	85
5	2.39	1.38	0.99	0.89	60	23	28	111
6	3.00	1.77	1.24	1.09	73	31	35	141
7	3.57	2.10	1.45	1.28	87	37	40	164
8	4.13	2.42	1.62	1.49	101	44	41	186
9	4.72	2.76	1.79	1.69	116	57	41	214
10	5.31	3.10	1.94	1.92	131	69	40	240
11	5.95	3.48	2.12	2.13	146	—	—	270
12	6.60	3.84	—	2.34	163	—	—	295
13	7.24	4.21	—	2.58	179	—	—	322
14	7.93	4.63	—	2.83	195	—	—	354
15	8.60	5.02	—	3.06	212	—	—	384
16	9.34	5.47	—	—	229	—	—	415

Accordingly, the χ-potential shift can be expressed as a function of HBr concentration in the form of a sum of the changes of two components: the adsorption potential due to the adsorbed undissociated HBr molecules (ΔE_{HBr}) and the adsorption potential due to the specifically adsorbed Br^- ions (ΔE_{Br^-}). The values of ΔE_{Br^-} can be estimated approximately from the χ-potential shift for water[56] under the influence of metal bromides, obtained with the aid of a voltaic cell of the type

$$Hg\,|\,Hg_2Cl_2\,|\,\text{sat. KCl. soln.}\,|\,MBr\,|\,\text{air}\,|\,\text{reference soln.}\,|\,\text{reference electrode.}\ \S$$

§Cell (B')? (Ed. of Translation).

Although the estimate of ΔE_{Br^-} for HBr solutions involves at least two gross assumptions (namely that the degrees of dissociation of HBr and metal bromides MBr are the same in equimolar solutions and that the liquid junction potentials in the above voltaic cell does not vary with MBr concentration), allowance for ΔE_{Br^-} in the calculation of pa_H^r from experimental data leads to satisfactory agreement between pa_H^r and the values of H_0, as can be seen from the data in Table 4. The results obtained for $HClO_4$ solutions were exactly the same (Table 5).

Table 5. The acidity functions pa_H^r and H_0, the adsorption potentials ΔE_{HA} and ΔE_{A^-}, the changes in the liquid junction potential ΔE_j in cell (B), and the compensating potentials $\Delta\epsilon$ in cell (B) for $HClO_4$–H_2O solutions at 25°C.

HA, mole %	$-pa_H^r$			$-H_0$	ΔE_{HA}, mV	ΔE_{A^-}, mV	ΔE_j, mV	$\Delta\epsilon$, mV
	pure solns.	solns. satd. with surface-active agent	with allowance for ΔE_{A^-}					
1	−0.10	−0.20	−0.20	−0.20	5	4	20	29
2	0.90	0.60	0.36	0.40	16	14	35	65
3	1.60	1.15	0.72	0.68	26	25	42	93
4	2.20	1.55	0.96	0.92	38	35	48	121
5	2.80	1.98	1.20	1.16	50	45	51	146
6	3.40	2.38	1.41	1.40	63	55	55	173
7	4.00	2.72	1.61	1.63	76	66	60	202
8	4.50	3.03	1.74	1.83	89	76	63	228
9	5.05	3.35	1.84	2.04	102	88	68	258
10	5.65	3.70	2.03	2.26	115	100	73	288
11	6.25	4.10	2.30	2.49	128	112	79	319
12	6.85	4.48	—	2.74	141	—	—	—
13	7.45	4.82	—	2.97	154	—	—	—
14	8.00	5.16	—	3.22	168	—	—	—
15	8.60	525.	—	3.47	183	—	—	—
16	9.20	5.85	—	3.73	—	—	—	—
17	9.75	6.18	—	3.99	—	—	—	—
18	10.40	6.50	—	4.25	—	—	—	—
19	11.00	6.83	—	4.55	—	—	—	—
20	11.65	7.23	—	4.86	—	—	—	—

Commenting on the results described[52,54], the following factors should be noted. The complete stabilisation of the χ-potential by non-ionogenic surface-active substances (particularly aliphatic alcohols) can be achieved only when there is no specific adsorption of the charged solution components and charged monolayers are not formed on the free solution surface. The question of the stabilisation of the surface potentials of solutions on the free surfaces of which charged species are specifically adsorbed remains open and its further investigation is extremely desirable. Furthermore, the changes $\Delta\epsilon$ for voltaic cells of type (B) as the acid concentration is varied can be divided into three components corresponding to the changes in the liquid junction potential ΔE_j, the adsorption potential ΔE_{HA} due to the molecular adsorption of acids and the adsorption potential ΔE_{A^-} due to the specific adsorption of the acid anions.

The results[52,54] yielded new information about the structure of the surfaces of solutions of strong inorganic acids. To explain the anomalously high adsorption shift of the χ-potential caused by strong acids, Randles suggested that H_3O^+ ions in the surface layer are preferentially oriented with the three H atoms directed towards the liquid phase. He believes that the other possible explanation, involving the preferential orientation of the ion pairs or undissociated acid molecules near the surface is unlikely, since $HClO_4$ and HI cause the greatest shifts of the χ-potential, while the dipole moments of these acids are smaller than that of HCl. The results presented in Tables 3, 4 and 5 show that, although $\Delta\epsilon$ for a cell of type (B) does decrease in the sequence $HClO_4 > HBr > HCl$, the quantity ΔE_{HA} increases in this sequence, which agrees with the increase in the dipole moments of the molecules on passing from HBr to HCl (the dipole moments of $HClO_4$ molecules are not available). Thus the experimental results support the hypothesis of the preferential orientation of the undissociated acid molecules in the surface layer.

The fact that the adsorption potentials of acids can be divided into molecular and ionic components (ΔE_{HA} and ΔE_{A^-}) using experimental data (on the basis of the non-thermodynamic assumption of the equality of the surface potentials of the stabilised solutions) suggests that the surface layers of solutions of strong acids consist of two sublayers. The upper sublayer adjoining the gas phase contains undissociated acid molecules with a preferential orientation of the dipoles such that the negative poles point towards the gas phase. These molecules may be hydrated. Ion pairs separated by solvent molecules are located in the lower sublayer with the same orientation of the dipoles. The monolayer of molecules of the surface-active agent on the solution–air interface screens the field generated by the acid and solvent dipoles in the upper sublayer. However, this sublayer does not constitute an obstacle to the electrostatic field generated by the ion pairs.

Table 6. The acidity functions pH, pa_H^r, and H_-, the adsorption potentials, the liquid junction potentials in cell (B), and the compensating potentials $\Delta\epsilon$ in cell (B) for NH_3–H_2O and N_2H_4–H_2O solutions at 25°C.

Concentration	$NH_3 - H_2O$					$N_2H_4 - H_2O$					
	pH	pa_H^r	$\Delta\epsilon$	ΔE_j	ΔE_{NH_3}	pH	pa_H^r	H_-	$\Delta\epsilon$	ΔE_j	$\Delta E_{N_2H_4}$
0.01	9.90	9.90	0	0	0	9.26	9.26	—	—	0	0
0.05	10.50	10.50	2	0	2	9.83	9.82	—	0	−1	1
0.1	10.74	10.74	8	0	8	10.09	10.07	—	1	−2	3
0.5	11.39	11.42	38	1	37	10.67	10.60	—	6	−5	11
1.0	11.60	11.65	75	3	72	10.94	10.84	—	17	−8	25
2.0	11.86	11.94	118	6	112	11.18	11.03	—	41	−9	50
3.0	12.00	12.14	155	9	146	11.42	11.25	—	65	−9	74
4.0	12.13	12.30	192	11	181	11.66	11.51	10.87	93	−8	101
5.0	12.24	12.47	217	14	203	11.86	11.73	11.45	114	−7	121
6.0	12.35	12.63	241	17	224	12.05	11.95	11.95	139	−6	145
7.0	12.47	12.79	262	20	242	12.25	12.17	12.42	162	−5	167
8.0	12.58	12.95	280	23	257	12.44	12.39	12.87	185	−3	188
10.0	12.80	13.27	313	27	286	12.79	12.87	13.55	228	+2	226
12.0	13.00	13.59	349	34	315	13.12	13.27	14.12	270	7	263
14.0	—	—	—	—	—	13.40	13.65	14.55	302	14	288
16.0	—	—	—	—	—	13.75	14.05	—	328	20	308
18.0	—	—	—	—	—	14.10	14.50	—	352	24	328

The stabilisation of the surface potentials of concentrated NH_3 and N_2H_4 solutions has been investigated[58,59] by the method used by Rybkin and Karpenko[52]. The surface-active agents employed were isopentyl and hexyl alcohols, hexylamine, and 1,1,3-tetramethylbutylamine. The use of these agents leads to similar values of ΔE_j and pa_H^r (Table 6). ΔE_j for NH_3–H_2O solutions does not vary greatly (only by 35 mV on passing from dilute solutions to 12 M NH_3 solution). Therefore, the real acidities of these media differ little from the pH. There are no literature values of the acidity functions H_0 or H_- for NH_3–H_2O solutions, which precludes a comparison of the results of the electrometric and indicator methods for the measurement of the acidity of the medium.

Table 7. The H_-, pH, and pa_H^r basicity scales for aqueous lithium, sodium, and potassium hydroxide solutions at 25°C.

Concn. of alkali, M	LiOH					NaOH					KOH			
	H_-^{61}	H_-^{62}	H_-^{63}	pH	pa_H^r	H_-^{61}	H_-^{64}	H_-^{65}	pH	pa_H^r	H_-^{61}	H_-^{64}	pH	pa_H^r
0.1	—	—	—	12.82	12.82	12.99	—	13.01	12.80	12.88	13.00	—	12.90	12.90
0.5	13.68	—	—	13.37	13.37	13.71	—	13.71	13.45	13.53	13.75	—	13.50	13.47
1.0	13.96	13.85	13.48	13.60	13.67	14.02	14.00	14.01	13.71	13.76	14.11	14.00	13.81	13.76
2.0	14.26	14.23	13.66	13.81	13.84	14.37	14.36	14.40	14.00	14.00	14.51	14.49	14.18	14.08
3.0	14.45	14.47	13.87	13.92	13.91	14.65	14.64	14.66	14.18	14.10	14.85	14.87	14.46	14.31
4.0	14.58	14.63	14.10	14.00	13.97	14.95	14.93	14.87	14.33	14.13	15.15	15.12	14.67	14.46
5.0	—	14.75	14.33	14.08	14.07	15.20	15.14	—	14.45	14.10	15.44	15.45	14.88	14.61
6.0	—	—	—	—	—	15.40	15.37	15.31	14.57	14.07	15.72	15.74	15.10	14.77
7.0	—	—	—	—	—	15.62	15.58	—	14.68	14.04	16.00	16.07	15.30	14.93

The ΔE_j for N_2H_4–H_2O solutions are negative at low concentrations, but their sign changes at concentrations above 10 M. As in NH_3–H_2O solutions, ΔE_j does not reach high values (about 25 mV in the 20 M solution), as a result of which the values of pa_H^r and pH are similar. However, they differ somewhat from the H_-.[60] The authors do not give a preference for any one of these acidity scales. Nevertheless, bearing in mind the results of Rybkin and Karpenko[54], the following remarks may be made. NH_3 and N_2H_4 solutions are extremely convenient for applying the method based on the stabilisation of the surface potential, since the ionisation of ammonia and hydrazine in the bulk of the solution and hence in the surface layer is insignificant. Because of this, it is extremely likely that the surface potentials of these solutions are completely equalised when they are saturated by surface-active agents. It also permits the assertion that the pa_H^r scale reflects most satisfactorily the concentration dependence of the acidity of the medium for the NH_3–H_2O and N_2H_4–H_2O systems.

The study of the stabilisation of the surface potentials of concentrated lithium, sodium, and potassium hydroxide solutions[59] yielded less clear-cut results owing to experimental difficulties caused by the salting-out of the surface-active substances in concentrated solutions of alkalis and by the poor wetting of the glass by the solutions saturated with the surface-active agent. Nevertheless, experiment showed that the shift of the χ-potential following the addition of the surface-active agents to the solutions of alkalis decreases in absolute magnitude with increased concentration of alkali. This indicates the stabilisation of the surface potentials of these solutions and presumably the stabilisation is fairly satisfactory, since OH^- ions show a smaller tendency towards specific adsorption at the solution–air interface compared with other ions. Furthermore, the adsorption of OH^- ions should be compensated to some extent by the specific adsorption of the cations. Comparison of the pa_H^r and pH scales with the known values of H_- [61–65] for concentrated lithium, sodium, and potassium hydroxide solutions (Table 7) shows that the indicator method yields unduly high values of the basicity of the medium. However, the insufficiency of experimental acidity data and the experimental difficulties in the study of the stabilisation of the χ-potentials of these media make it so far impossible to give preference to any of the acidity scales mentioned above.

The stabilisation of the χ-potential of the HCOOH–H_2O system has been studied[66,67] by means of a voltaic cell of type (A′). Caproic and oenanthic acids were used as surface-active agents, because the employment of alcohols is undesirable owing to the possible formation of esters. Like the NH_3 and N_2H_4 solutions, HCOOH–H_2O mixtures are suitable for the application of the surface potential stabilisation method, since HCOOH is a moderately strong acid and therefore the specific adsorption of anions in the surface layer should be significant. A constant amount of added caproic and oenanthic acids (0.1 and 0.03 mole % respectively) stabilises the χ-potentials of the HCOOH–H_2O mixtures, as shown by the markedly different acidity functions pa_H^r obtained for the pure HCOOH–H_2O mixtures and for the same mixtures containing the surface-active agent (Table 8). Table 8 also lists the acidity functions H_0 [68] and the pH. The results in Table 8 show that the pa_H^r differ sharply from the corresponding values of the other functions, indicating a higher acidity of the medium than that given by the other functions.

Table 8. The acidity functions pa_H^r, pH, and H_0, the compensating potentials in cell (B), the adsorption potentials of formic acid, and the liquid junction potentials in cell (B) for HCOOH–H_2O solutions at 25°C.

HCOOH, mole %	$-pa_H^r$		−pH	$-H_0^*$	Δε, mV	ΔE_{HA}, mV	ΔE_j, mV
	pure HCOOH solns.	solns. satd. with surface-active agent					
0.5	−2.14	−2.14	−2.15	—	−1	0	−1
5.0	−0.78	−0.74	−1.47	−1.49	−41	3	−43
10.0	−0.22	0.63	−1.13	−1.39	−54	50	−104
15.0	0.18	1.98	−0.88	−1.13	−60	107	−167
20.0	0.62	3.22	−0.54	−0.98	−68	154	−222
25.0	0.96	4.30	−0.26	−0.85	−72	198	−270
30.0	1.22	5.22	0.00	−0.70	−72	237	−309
40.0	1.63	6.59	0.47	−0.43	−69	294	−362
50.0	1.96	7.42	0.89	−0.14	−63	323	−386
60.0	2.34	7.91	1.32	+0.19	−61	329	−390
70.0	2.81	8.28	1.77	0.50	−62	323	−385
80.0	3.41	8.76	2.30	0.84	−66	316	−382
90.0	4.12	9.49	2.92	1.22	−72	317	−389
100	4.89	10.47	3.67	2.19	−72	330	−402

*Interpolated from literature data[68].

The following comments may be made concerning Table 8. The known values[69] of the adsorption shift of the χ-potentials of water caused by aliphatic carboxylic acids (ranging from formic to caproic) are listed without correction for the change in the liquid junction potential in a cell of type (B). These data create the impression of an anomalous behaviour of formic acid, the addition of which

to water causes a negative shift of the χ-potential [negative values of Δε for a cell of type (B) in Table 8], while the addition of the remaining acids of the same homologous series leads to a corresponding shift in the opposite direction. The results[66,67] compiled in Table 8 show that the adsorption behaviour of formic acid at the solution–air interface is not anomalous: the corresponding function ΔE_{HA} assumes positive values, reaching almost 330 mV, which is extremely close to the corresponding values of this function for butyric, valeric, and caproic acids (349, 355, and 340 mV respectively)[69]. The negative values of Δε for a voltaic cell of type (B) are caused by the fact that the liquid junction potential in this cell shifts faster than ΔE_{HA} and in the opposite direction, reaching a value of about 400 mV for concentrated formic acid.

It is striking that, in the range of compositions from 0 to 35 mole % HCOOH, there is a sharp variation of both ΔE_j and the acidity of the medium. For this reason, in a cell of type (B′) the concentration variation of the potential of the hydrogen electrode, due to the changes in the acidity of the medium, is partly compensated by the corresponding variation of ΔE_j. As a result, measurements using cells of type (B′) lead to low pH values, which incorrectly reflect the acidity of the $HCOOH-H_2O$ solutions. Low Hammett acidity functions H_0 have also been observed for such solutions[68], but the reason for this has not been established accurately. They are probably caused by the specific interaction of the indicator base, used for the measurement of H_0, with formic acid, of the type observed by Kolthoff and coworkers[70].

Table 9. The acidity functions pa_H^r and pH, the adsorption potentials of acetic acid, and the changes in the compensating potential and the liquid junction potential in cell (B) for 0.01 M HCl solutions in $CH_3COOH-H_2O$ mixtures at 25°C.

CH_3COOH, mole %	pa_H^r		pH	Δε, mV	ΔE_{HA}, mV	ΔE_j, mV
	pure solns.	solns. with added oenanthic acid				
0	2.10	2.10	2.10	—	—	—
1	4.00	1.95	2.04	127	121	5
2	4.66	1.80	1.97	179	169	10
4	5.23	1.50	1.86	242	221	21
6	5.57	1.20	1.76	292	259	33
8	5.81	0.95	1.68	331	288	43
10	5.93	0.80	1.60	351	304	47
12	5.94	0.75	1.50	351	307	44
15	5.91	0.70	1.40	350	308	42
20	5.89	0.60	1.22	350	313	37
30	5.73	0.40	0.86	342	315	27
40	5.42	0.15	0.46	330	312	18
50	5.05	−0.15	0.02	318	308	10
60	4.66	−0.55	−0.50	311	308	3
70	4.18	−1.20	−1.15	315	318	−3
80	3.58	−1.90	−2.00	318	324	−6
90	2.84	−2.50	−2.85	295	316	−21
100*	2.00	−3.25	−3.80	282	315	−33

*Found by extrapolation.

The stabilisation of the χ-potentials of 0.01 M HCl solutions in acetic acid–water mixtures has been studied[71]. The results are compiled in Table 9. The values for 100% acetic acid were obtained by extrapolation. The surface-active agent (caproic acid) stabilises the surface potentials of the solutions (at least at low acetic acid concentrations), as shown by the markedly different values of pa_H^r for the pure solutions and the solutions stabilised by caproic acid. The function ΔE_{HA} for acetic acid assumes positive values, reaching approximately 320 mV, which is a little less than the corresponding values for formic[66,67], butyric, valeric, and caproic acids[69].

As for $HCOOH-H_2O$ mixtures, a fairly sharp variation of the acidity of the medium and of the liquid junction potential in a cell of type (B) at low acetic acid concentrations (up to 10 mole %) is characteristic of $CH_3COOH-H_2O$ mixtures and these two effects again partly cancel out, as a result of which the pH of these solutions, determined with the aid of cells of type (B′), varies more slowly with solvent composition than pa_H^r. According to Schwarzenbach and Stensby[72], H_0 varies even more slowly. At high acetic acid concentrations, pH overtakes pa_H^r. This may be associated with the unusual dependence of the liquid junction potential on solvent composition, the potential shifting towards negative values at low acetic acid concentrations, reaching a minimum of 10–15 mole% of acetic acid and then slowly shifting towards positive values at high concentrations. This behaviour of ΔE_j appears strange and may be associated with an experimental error. This is suggested also by the finding that the ΔE_{HA} function for acetic acid does not reach values characteristic of caproic and other carboxylic acids and the ΔE_{HA}–composition curve for the $CH_3COOH-H_2O$ mixtures passes through a maximum. At high acetic acid concentration the introduction of caproic acid into the solutions probably does not adequately stabilise the surface potential. The problem of the stabilisation of the χ-potential in the $CH_3COOH-H_2O$ system requires further study.

Table 10. The compensating and liquid junction potentials in cell (B), the adsorption potentials of CH_3OH, and the $\lg \gamma^{\circ r}_{H^+}$ for hydrogen ions in dilute HCl solutions in CH_3OH-H_2O mixtures at 25°C.

CH_3OH, mole %	Δε, mV	ΔE_j, mV	ΔE_{CH_3OH}, mV	$\lg \gamma^{\circ r}_{H^+}$	CH_3OH, mole %	Δε, mV	ΔE_j, mV	ΔE_{CH_3OH}, mV	$\lg \gamma^{\circ r}_{H^+}$
2	107	7	100	0.12	40	344	58	286	1.12
4	168	13	155	0.20	50	353	66	288	1.25
6	201	17	184	0.29	60	360	73	287	1.31
8	230	21	209	0.36	70	365	79	286	1.27
10	248	24	224	0.41	80	369	84	285	1.02
20	301	39	262	0.70	90	372	89	283	0.72
30	328	50	278	0.93	100	375	93	282	0.77

The assumed constancy of the surface potential has been used to determine the medium effects of H^+ ions on passing from water to methanol[73]; the surface potentials of dilute HCl solutions in aqueous alcoholic solvents were stabilised by heptyl alcohol. The results are illustrated in Table 10. As regards certain features, they resemble the results for $HCOOH-H_2O$ and $CH_3COOH-H_2O$ mixtures. In particular, at low methanol concentrations in the solvent both the acidity of the medium (pa_H^r) and the liquid junction potential vary sharply. Therefore, in a cell of type (B′) the shift of the hydrogen electrode potential due to the change in the acidity of the medium is overlapped by the corresponding more marked shift of ΔE_j, as a result of which the pH values measured with the aid of this cell yield incorrect information about the acidity of the aqueous alcoholic HCl solutions. In contrast to the

behaviour of the HCOOH–H_2O and CH_3COOH–H_2O mixtures, small amounts of added organic solvent do not increase but actually decrease the acidity of the medium and the liquid junction potential shifts towards positive values rather than to negative values.

The above features and also the results discussed previously for the HCl–H_2O, $HClO_4$–H_2O, HBr–H_3O, NH_3–H_2O, and N_2H_4–H_2O systems suggest that there is at least a qualitative correlation between the variation of the acidity of the medium and the corresponding variation of the liquid junction potential: an increase of acidity is accompanied by a shift of the liquid junction potential towards negative values, while a decrease of acidity corresponds to a positive shift of ΔE_j. In other words, with decreased basicity of the medium, the tendency of H^+ ions to cross the test solution–saturated KCl solution interface is weaker than for ions of the opposite sign. However, a quantitative correlation cannot be observed. It is appropriate to mention here that the idea of a relation between the acid–base interactions in solutions and the anomalous mechanism of charge transfer by H^+ ions has already been suggested in the literature [74]. Continuing the analysis of the results of experiments on the stabilisation of the χ-potentials of aqueous alcoholic HCl solutions, mention must be made of the fact that there is a qualitative agreement between the results obtained from the analysis of the dependence of the functions $\lg \gamma^{\circ r}_{H^+}$, $\lg \gamma^{\circ}_{H^+}$, and H_0 on the composition of the aqueous alcoholic solvent [8,55]. The sharp decrease of the acidity of the medium following the addition of small amounts of methanol to water is consistent with the changes in the other volume properties of electrolytes in alcohol–water mixtures and with the changes in the volume properties of the mixtures themselves, which can be explained by the stabilisation of the water structure in the presence of alcohol molecules [75,76].

It is known that the addition of inorganic salts to water usually leads to an increase in the surface tension of the solutions formed, as a result of which the surface layers of such solutions are depleted in the electrolyte. According to the calculations of a number of investigators [77,78], the thickness of the surface layer free from the electrolyte ranges from 3 to 5 Å for dilute aqueous solutions of strong electrolytes. This suggests that the surface potentials of electrolyte solutions, whose ions exhibit a weak tendency towards specific adsorption at the solution–air interface, do not differ significantly from the surface potential of pure water. This is valid also for fairly dilute solutions of weak electrolyte, which are not very active at the solution–air interface. If this is true, the voltaic cells of type (A) or (A′) can be used to compare the activities of individual ions (in particular the medium acidities) in such solutions or to estimate ΔE_j without introducing into the test solutions surface-active agents in order to stabilise the surface potential. Direct evidence for the weak influence of electrolytes on the surface potentials of solutions has been published [79–81]. The acidities of standard buffer solutions have been compared without the stabilisation of the potentials [82] and it has been shown that the values of pa^r_H obtained using a voltaic cell of type (A) do not differ from the corresponding values of pa_H (to within 0.02). A standard hydrogen phthalate buffer solution was an exception for reasons which are not altogether clear; according to the results of Kamienski et al [83] both potassium hydrogen phthalate and phthalic acid are surface-active.

The acidities of dilute HCl solution and standard buffer solutions have been compared in the presence of high concentrations of neutral salts [84,85]. The main result of these studies is that the values of pa^r_H and pH agree over fairly wide ranges of the concentrations of the supporting salt. Thus pH and pa^r_H for 0.01 M HCl solution agree up to LiCl, NaCl, and KCl concentrations of 3.5, 3.0, and 1.5 M respectively. The discrepancies between pH and pa^r_H at higher concentrations of the neutral salts can be naturally accounted for by a shift of the χ-potential of the solution due to the appearance of electrolyte ions in the surface layer. Then anions, which are less hydrated, are on average distributed closer to the solution–air interface than cations. A definite inference can be drawn about the diffusion potential at the interfaces between concentrated salt solutions and the saturated KCl solution. The agreement between pH and pa^r_H over a fairly wide range of concentrations of the neutral salts suggests that the diffusion potential varies little with salt concentration and the measurements of the pH of salt solutions in cells with transport are fairly reliable. One should not expect an appreciable effect of acidity on ΔE_j in concentrated salt solutions, of the kind observed in the systems discussed above, since charge transfer across the liquid junction is effected by the salt ions and not H^+ ions.

In conclusion the following remarks may be made. The technique involving the stabilisation of the surface potentials of solutions makes it possible to obtain information about the thermodynamic characteristics of individual ions and liquid junction potentials, which are in good agreement with data found by other non-thermodynamic methods. In many cases this makes it possible to obtain completely new data (for example, for the HCOOH–H_2O, CH_3COOH–H_2O, NH_3–H_2O, and N_2H_4–H_2O systems), which had been hitherto outside the scope of other methods. The technique involving the stabilisation of the χ-potentials of solutions yields fairly accurate values of the adsorption potentials of a number of substances (for example, HCl, HBr, $HClO_4$, HCOOH, CH_3COOH, CH_3OH, NH_3, and N_2H_4) at the solution–air interface, which until now could not be achieved owing to the miscibility of these substances with water and owing to the influence of the liquid junction potentials. The knowledge of the adsorption potentials makes it possible to set up a scale of χ-potentials for a number of solvents and media (adopting as the zero point for the readings the χ-potential of water, the absolute value of which is not yet known reliably): CH_3OH (280–290 mV); HCOOH (320–330 mV); CH_3COOH (320–350 mV); 20 mole % HCl–H_2O (about −350 mV); 25 mole % HBr–H_2O (about −210 mV); 10 mole % $HClO_4$–H_2O (about −115 mV); 10 mole % NH_3–H_2O (about 290 mV); 18 mole % N_2H_4–H_2O (about 330 mV). The χ-potential scale may prove useful in the derivation of information about the chemical potentials of individual ions on the basis of the experimental values of the real potentials of these ions.

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