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Salt Effects of Potassium Nitrate, Sodium Sulfate, and Trisodium Citrate on the Activity Coefficients of *p*-Phenolsulfonate Buffers

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Electromotive-force measurements of cells without liquid junction that contained hydrogen and silver–silver-chloride electrodes and alkaline *p*-phenolsulfonate buffers with added salts of different valence types were made from 0° to 60° C. The 63 buffer solutions studied were prepared by the partial neutralization of potassium *p*-phenolsulfonate with sodium hydroxide, and each contained approximately equal molal amounts of potassium *p*-phenolsulfonate and of potassium sodium *p*-phenolate sulfonate. These solutions were classified into five series on the basis of the kind of added salt and the ratio, R, of its molality to the molality of each buffer salt, as follows: Potassium nitrate, $R=1$; sodium sulfate, $R=1$; sodium sulfate, $R=0.5$; barium chloride, $R=0.5$; trisodium citrate, $R=0.33$. All the buffers, with the exception of the series to which barium chloride was added, likewise contained sodium chloride, $R=1$. The ionic strengths of the solutions varied from 0.05 to 0.8.

The values of the second dissociation constant of *p*-phenolsulfonic acid given in an earlier paper were confirmed. The influence of potassium nitrate, sodium sulfate, and trisodium citrate on the activity coefficient term, $f_{\mathrm{Cl}}f_{\mathrm{HPs}}/f_{\mathrm{Ps}}$, in which f represents an activity coefficient on the molal scale and the subscripts represent respectively chloride ion and the primary and secondary anions of the buffer, was determined for solutions containing no sodium chloride at 0° to 35° C. No pronounced differences in character were observed among the effects of the salts of the three valence types in concentrations sufficient to make up one-fifth of the ionic strength of the mixture.

I. Salt Effect on the pH of Buffered Solutions

Addition of a neutral salt to a buffer solution composed of the primary and secondary salts of a weak dibasic or polybasic acid normally results in an increase in the acidity of the solution. Inadequate knowledge of the activity coefficients in mixtures of electrolytes and of their role in the behavior of a system in homogeneous equilibrium however, often makes it impossible to predict quantitatively the effect of salt on the pH.

The pH of a buffer composed of potassium *p*-phenolsulfonate (KHPs) and of potassium sodium *p*-phenolate sulfonate (KNaPs) can be expressed by the mass-law equation in loga-

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rithmic form, with the appropriate activity coefficients, as follows:

$$\mathrm{pH} = \mathrm{p}K - \log\,(m_{\mathrm{HPs}}/m_{\mathrm{Ps}}) - \log(f_{\mathrm{HPs}}/f_{\mathrm{Ps}}), \quad (1)$$

where pK is the negative of the common logarithm of the dissociation constant of the phenol group of p-phenolsulfonic acid on the molal scale, m represents molality (moles/1,000 g of water), and f is the activity coefficient on the corresponding scale. It is evident that the change of pH with addition of neutral salt to a phenolsulfonate buffer must result largely from changes in the activity coefficients of the two anions of the buffer.

The change in pH when salt is added to the buffer solution is called the total salt effect. If provision is made for the effect of hydrolysis upon the molal ratio (second term on the right of eq 1), and the molalities of the components of the buffer remain unaltered, the change of the last term of eq 1 upon addition of salt measures the total salt effect.

It may reasonably be supposed that the change of the activity-coefficient term when the ionic strength of the solution changes at constant buffer ratio as a result of a variation in buffer concentration alone can be expressed by an equation such as the following:

$$\log \frac{f_{\mathrm{HPs}}}{f_{\mathrm{Ps}}} = \frac{3A\sqrt{\mu}}{1+Ba\sqrt{\mu}} + \beta\mu, \quad (2)$$

where A and B are constants of the Debye-Hückel equation, μ is the ionic strength, and a and β are parameters characteristic of the mixture of ions. The values of a and β evidently control the rate of change of log $(f_{\mathrm{HPs}}/f_{\mathrm{Ps}})$ with ionic strength and, hence, the total salt effect. When neutral salt is added to a buffer solution, the character of the variation of the activity-coefficient term with ionic strength may be unaffected. On the other hand, a and β may change as a result of interactions of the buffer ions with those of the salt, and the variation with ionic strength will then be different.

The total salt effect, therefore, can be of two types. The effect of salt addition is of the first type when the change of pH produced is the same as would normally result from an increase in ionic strength of the buffer alone, without the introduction of foreign ions or molecules. Thus, the pH of the mixture of buffer and salt will be the same as that of a more concentrated buffer of the same ionic strength and buffer ratio, without added salt. In other words, the rate of change of the activity-coefficient term with ionic strength remains unaltered when a neutral salt is substituted for an amount of buffer mixture which contributes the same increment to the ionic strength.

The second type of salt effect is the result of specific or abnormal interactions among the ions of the mixture. In the extreme case, these interactions may alter not only the activity coefficients of the buffer ions but their concentrations as well. Polar compounds, polymers, or complex ions may even be formed. These effects cause the activity-coefficient term to change in an abnormal manner with changing ionic strength. As a result, the pH of the buffer with salt differs from that of a pure buffer solution of the same ionic strength and buffer ratio.

In most cases, the effect of salt is probably of the more general second type. Furthermore, the term log $(f_{\mathrm{HPs}}/f_{\mathrm{Ps}})$ at constant ionic strength may reasonably be expected to vary linearly with composition of the solution. When the kinds of ions added are similar to those of the buffer, however, it is possible that they will alter the activity-coefficient term by the same amount as would the buffer ions, added in like quantity. A salt effect of the second type may, of course, appear to be of the first type when the amount of salt added is small compared with the ionic strength of the buffer itself.

The problem of determining salt effects on the phenolsulfonate buffer is resolved into a determination of the changes in the activity coefficients on addition of salt. Unfortunately, the ratio of the activity coefficients of the primary and secondary anions, $f_{\mathrm{HPs}}/f_{\mathrm{Ps}}$, cannot readily be measured. In this investigation, the character of the salt effect of potassium nitrate, sodium sulfate, and trisodium citrate on the activity coefficients of these ions was studied by evaluating the activity-coefficient term, $f_{\mathrm{HPs}}f_{\mathrm{Cl}}/f_{\mathrm{Ps}}$, in buffered solutions of sodium chloride with and without one of the three neutral salts. In order that the observed effect might represent as closely as possible the influence of the salt on the buffer ions alone, the activity-coefficient term was evaluated in the limit of zero sodium chloride from 0° to 35° C.

Electromotive-force measurements at 0° to 60° C were made with buffer mixtures composed of sodium chloride and approximately equal molal amounts of potassium p-phenolsulfonate and potassium sodium *p*-phenolate sulfonate without added salt, and for similar buffers which contained potassium nitrate, sodium sulfate, or trisodium citrate. One series contained barium chloride instead of sodium chloride. The effects of the three alkali salts of different valence types on the activity coefficients were found to be approximately the same when the added salt made up one-fifth of the total ionic strength. The emf data for these buffer solutions with added salt, together with those for the series of buffers that contained chloride, confirm the values for the second dissociation constant of *p*-phenolsulfonic acid found in an earlier study [1].[1]

II. Method of Evaluating the Effect of Salts on the Activity Coefficients

Electromotive-force measurements of cells of the type

$$\text{Pt-H}_2\,|\,\text{KHPs}(m_1);\ \text{KNaPs}(m_2);\ \text{NaCl}(m_3);\ \left.\left\{\begin{matrix}\text{KNO}_3\\ \text{Na}_2\text{SO}_4\\ \text{BaCl}_2\\ \text{Na}_3\text{C}_6\text{H}_5\text{O}_7\end{matrix}\right\}\right.(m_4)\,|\,\text{AgCl-Ag} \qquad \text{(I)}$$

were made at intervals of 5 degrees from 0° to 60° C. The chemical changes that result from drawing a finite current from this cell are given by the complete cell reaction,

$$1/2\text{H}_2+\text{AgCl}+\text{Ps}^{=}=\text{Ag}+\text{Cl}^{-}+\text{HPs}^{-}, \qquad (3)$$

for which the standard free energy change, $-\Delta F^{\circ}*$, is

$$-\Delta F^{\circ}*=E^{\circ}*\boldsymbol{F}=RT\ln K^{*}, \qquad (4)$$

where $E^{\circ}*$ is the potential of the hypothetical cell of type I, in which each of the components has an activity of unity; K^* is the thermodynamic equilibrium constant for eq 3; and R, T, and $\boldsymbol{F}$ are the gas constant, the absolute temperature, and the faraday.

The total reaction in the cell may be written in two parts. The first of these is the electrode reaction,

$$1/2\text{H}_2+\text{AgCl}=\text{Ag}+\text{H}^{+}+\text{Cl}^{-};\ -\Delta F_1^{\circ}=E^{\circ}\boldsymbol{F}, \qquad (5)$$

where E° is the standard potential of the cell, $\text{H}_2|\text{HCl}|\text{AgCl-Ag}$, and the other is a homogeneous equilibrium that involves the hydrogen ion formed by the electrode reaction, namely, the equilibrium between the primary and secondary anions of phenolsulfonic acid,

$$\text{HPs}^{-}=\text{H}^{+}+\text{Ps}^{=};\ -\Delta F_2^{\circ}=RT\ln K. \qquad (6)$$

The constant K in eq 6 is the thermodynamic second dissociation constant for the acid. It has been determined by Bates, Siegel, and Acree [1] over the range of temperatures from 0° to 60° C. From eq 4, 5, and 6 it is evident that

$$\begin{aligned}E^{\circ}*&=E^{\circ}-(RT/\boldsymbol{F})\ln K\\ &=E^{\circ}+(2.3026\,RT/\boldsymbol{F})\text{p}K,\end{aligned} \qquad (7)$$

where pK is the negative of the common logarithm of K. Values of E° at 0° to 60° C have been recalculated by Hamer, Burton, and Acree [2] from the emf data of Harned and Ehlers [3].

The relation between emf, E, and the molalities and activity coefficients of the reactants and products of the cell reaction is

$$\frac{E-E^{\circ}*}{k}+\log\frac{m_{\text{HPs}}m_{\text{Cl}}}{m_{\text{Ps}}}=-\log\frac{f_{\text{HPs}}f_{\text{Cl}}}{f_{\text{Ps}}}, \qquad (8)$$

where k is written for 2.3026 $RT/\boldsymbol{F}$. The activity-coefficient term in the equilibrium constant for reaction 3 can be computed from the emf by eq 8. By observing the behavior of the emf and, through it, the activity-coefficient term when neutral salts of different valence types are added to the buffered chloride solutions, information can be gained regarding the nature of the effect of added salt on the three ions involved in the cell reaction.

In solutions that contained neutral salts, as in buffered chloride solutions without added salts [4], the experimental values of the last term of eq 8 could be represented satisfactorily by an equation of the type

$$\log\frac{f_{\text{HPs}}f_{\text{Cl}}}{f_{\text{Ps}}}=\frac{2A\sqrt{\mu}}{1+Ba^{*}\sqrt{\mu}}+\beta^{*}\mu, \qquad (9)$$

derived from the Debye-Hückel theory. Inasmuch as a confirmation of the value of pK was desired, a^* and β^* were evaluated as before [1] from the graphs used to derive this constant by extrapolation of the values of pK', the negative logarithm of the "apparent" dissociation constant, to an ionic strength of zero.

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[1] Figures in brackets indicate the literature references at the end of this paper.

pK' is defined through a combination of eq 7, 8, and 9:

$$\mathrm{p}K'=\mathrm{p}K-\beta^*\mu=\frac{E-E^\circ}{k}+\log\frac{m_{\mathrm{HPs}}m_{\mathrm{Cl}}}{m_{\mathrm{Ps}}}+\frac{2A\sqrt{\mu}}{1+Ba^*\sqrt{\mu}}. \tag{10}$$

In the range of temperatures from 0° to 35° C, a^* and β^* were also determined for phenolsulfonate buffers with and without neutral salt at several different concentrations of sodium chloride. The values of these parameters were plotted as a function of m_{NaCl}/μ, the fractional contribution of sodium chloride to the ionic strength, and the corresponding values, a° and β°, in the absence of sodium chloride were obtained by extrapolation. The value of the activity-coefficient term in the limit of zero sodium chloride, f°_R, is defined by

$$\log f^\circ_R\equiv\log\left[\frac{f_{\mathrm{HPs}}f_{\mathrm{Cl}}}{f_{\mathrm{Ps}}}\right]_{m_{\mathrm{Cl}}=0}=\frac{2A\sqrt{\mu}}{1+Ba^\circ\sqrt{\mu}}+\beta^\circ\mu. \tag{11}$$

It is impossible to compute the change of pH upon addition of salt to the buffer solution from the measured change in f°_R without recourse to an arbitrary assumption regarding the relative magnitudes of the individual activity coefficients. The parameters a° and β° might, for example, be identified with a and β of eq 2, or a relation such as $\log f_{\mathrm{Cl}}=-(1/3)\log(f_{\mathrm{HPs}}/f_{\mathrm{Ps}})$, based upon valence effects in very dilute solutions, be introduced. The influence of neutral salt on $\log f^\circ_R$ should, however, approximate in character the salt effect on the buffer anions alone. From these results, therefore, an estimate could be made of (a) the magnitude of the change in the activity-coefficient term of eq 1 when small concentrations of salt are added to the buffer and (b) whether salts of different types produce markedly different effects on the pH, apart from their different contributions to the ionic strength.

III. Experimental Procedures and Results

The buffer solutions were made by the weight dilution of stock solutions that were prepared in quantities of two liters each from weighed amounts of potassium *p*-phenolsulfonate and a standard solution of carbonate-free sodium hydroxide. Each stock solution, with the exception of the one to which barium chloride was added, also contained both sodium chloride and one of the three neutral salts[2] chosen for study. The specific conductance of the water was in most cases about 0.5×10^{-6} mho.

The potassium phenolsulfonate analyzed 100.10 percent by titration with alkali. The sodium chloride was part of the same fused sample used in earlier work on phenolsulfonate buffers [1, 4]. It was found by titration with acid to contain 0.007 percent by weight of free alkali. This amount of impurity changes the emf of the cell by less than 0.01 mv and can safely be ignored. Description of the equipment, methods of preparing the electrodes, and other experimental details have been given elsewhere [1, 5].

The emf data for cell I are given in the sections to follow. In each of the 63 buffers, m_1 and m_2 were approximately equal. When sodium chloride was present, its molality was usually nearly the same as that of each buffer salt, except in series F, where the ratio of chloride to buffer was varied. The ratio, R, of m_4 to m_1 was approximately unity for solutions that contained potassium nitrate, 1 and 0.5 for sodium sulfate, and 0.33 for trisodium citrate. Sodium chloride was absent from series D, and barium chloride ($R=0.5$) was present.

The combined experimental errors in the compositions of the solutions and in the emf measurements, together with the errors in the values of the natural constants and the standard potential, are thought not to exceed 0.18 mv at any temperature. The uncertainty from these sources amounts to 0.003 in the activity-coefficient term of eq 9 or eq 11.

1. Buffers With Added Potassium Nitrate

Potassium nitrate of reagent quality was recrystallized once from water and dried to constant weight at 110° C. Preliminary experiments showed that satisfactory results could be obtained with the hydrogen electrode in solutions that contained nitrate ion in moderate concentration in a phenolsulfonate buffer at a pH of 8.8. The hydrogen electrodes in solutions containing 0.06- to 0.1-m potassium nitrate, however, oc-

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[2] A neutral salt is considered here to be one that has no appreciable buffer capacity at pH 8.4 to 9.2. Inasmuch as hydrogen and silver-silver-chloride electrodes were used, chlorides, bromides, iodides, sulfides, and substances readily reduced by hydrogen in alkaline solution were excluded.

casionally gave erratic potentials and had to be replaced. No larger differences between the initial and final emf at 25° C were found, however, with nitrates than with other salts, and the dilute solutions were satisfactory in every respect. The emf results for 1:1 buffers with added potassium nitrate are given in table 1.

TABLE 1.—*Electromotive forces of hydrogen–silver-chloride cells containing mixtures of potassium p-phenolsulfonate* (m_1), *poiassium sodium p-phenolate sulfonate* (m_2), *sodium chloride* (m_3), *and potassium nitrate* (m_4)

[$m_2=0.9785m_1$; $m_3=0.9349m_1$; $m_4=0.9332m_1$]

Solution number	m_1	E_0°	E_5°	E_{10}°	E_{15}°	E_{20}°	E_{25}°	E_{30}°	E_{35}°	E_{40}°	E_{45}°	E_{50}°	E_{55}°	E_{60}°
A1	0.10830	0.78654	0.78003	0.79339	0.79676	0.79998	0.80319	--------	0.80932	0.81264	0.81570	0.81901	0.82204	0.82503
A2	.08572	.79168	.79534	.79874	.80232	.80571	.80910	--------	.81558	.81904	.82217	.82555	.82879	.83211
A3	.04450	.80721	.81123	.81510	.81896	.82238	.82675	0.83042	--------	.83732	.84114	.84516	.84885	.85248
A4	.03591	.81270	.81690	--------	.82457	.82856	.83269	.83659	--------	.84407	.84785	.85188	.85562	.85930
A5	.02520	.82172	.82609	.83027	.83450	.83856	.84263	.84670	.85055	.85454	.85859	.86261	.86654	.87046
A6	.013753	.83706	.84176	.84626	.85079	.85511	.85958	.86392	.86801	.87253	.87670	.88096	.88512	.88930
A7	.011864	.84087	.84559	.85019	.85476	.85927	.86374	.86821	.87239	.87697	.88121	.88510	.88982	.89409
A8	.008651	.84873	.85352	.85844	.86319	.86785	.87258	.87725	.88157	.88635	.89177	.89534	.89977	.90423

2. Buffers with added sodium sulfate

Sodium sulfate, of the grade designated "for nitrogen determination", was recrystallized twice from water. The water of hydration was removed by drying the salt in a vacuum oven at temperature up to 100° C and at 130° C under atmospheric pressure. Two ratios of anhydrous sodium sulfate to buffer were studied. The buffers of series B contained approximately equal molal amounts of sodium sulfate and of each buffer salt, whereas the five solutions in series C contained one-half as much added salt as buffer. The emf values at 0° to 60° C are given in table 2.

3. Buffers with Added Barium Chloride

Measurements were made of one series of phenolsulfonate buffers in which barium chloride was substituted for sodium chloride. The method outlined earlier in this paper obviously cannot serve to determine the salt effect of barium chloride on

TABLE 2.—*Electromotive forces of hydrogen–silver-chloride cells containing mixtures of potassium p-phenolsulfonate* (m_1), *potassium sodium p-phenolate sulfonate* (m_2), *sodium chloride* (m_3), *and sodium sulfate* (m_4).

[Solutions B1 to B5: $m_2=0.9916m_1$; $m_3=0.9425m_1$; $m_4=0.9727m_1$. Solutions B6 to B11: $m_2=1.0150m_1$; $m_3=0.9512m_1$; $m_4=0.9554m_1$. Solutions B12 to B20: $m_2=0.9803m_1$; $m_3=0.9455m_1$; $m_4=0.9444m_1$. Series C: $m_2=0.9743m_1$ $m_3=0.9413m_1$; $m_4=0.4732m_1$]

Solution number	m_1	E_0°	E_5°	E_{10}°	E_{15}°	E_{20}°	E_{25}°	E_{30}°	E_{35}°	E_{40}°	E_{45}°	E_{50}°	E_{55}°	E_{60}°
B1	0.10686	--------	--------	--------	--------	--------	0.80234	0.80569	0.80883	--------	--------	--------	--------	--------
B2	.06602	--------	--------	--------	--------	--------	.81520	.81876	.82234	--------	--------	--------	--------	--------
B3	.05438	--------	--------	--------	--------	--------	.82054	.82420	.82782	--------	--------	--------	--------	--------
B4	.02030	--------	--------	--------	--------	--------	.84785	.85207	.85634	--------	--------	--------	--------	--------
B5	.010524	--------	--------	--------	--------	--------	.86636	.87092	.87542	--------	--------	--------	--------	--------
B6	.10443	0.78644	0.78993	0.79333	0.79672	0.80007	.80339	.80676	.81002	0.81330	0.81652	0.81973	0.82287	0.82609
B7	.06808	.79660	.80032	.80407	.80772	.81130	.81490	.81852	.82201	.82551	.82895	.83235	.83576	.83914
B8	.04623	.80607	.81007	.81393	.81776	.82154	.82535	.82912	.83284	.83655	.84016	.84375	.84741	.85097
B9	.02709	.81939	.82377	.82793	.83205	.83619	.84030	.84440	.84838	.85237	.85631	.86020	.86407	.86792
B10	.013336	.83763	.84232	.84684	.85134	.85580	.86027	.86467	.86903	.87336	.87768	.88196	.88616	.89038
B11	.013036	.83798	.84271	.84725	.85172	.85620	.86073	.86508	.86948	.87389	.87802	.88213	.88634	.89016
B12	.10722	.78516	.78866	.79216	.79557	.79872	.80207	.80535	.80861	.81193	.81508	.81827	.82140	.82450
B13	.08036	.79189	.79553	.79918	.80281	.80618	.80965	.81308	.81656	.82000	.82330	.82669	.83001	.83332
B14	.06067	.79879	.80261	.80641	.81012	.81365	.81731	.82087	.82444	.82805	.83155	.83501	.83844	.84189
B15	.04181	.80796	.81197	.81598	.81993	.82366	.82749	.83128	.83506	.83885	.84252	.84621	.84986	.85351
B16	.02823	.81766	.82190	.82612	.83029	.83430	.83832	.84238	.84637	.85036	.85424	.85814	.86200	.86583
B17	.015906	.83247	.83701	.84148	.84597	.85028	.85462	.85894	.86321	.86756	.87177	.87597	.88012	.88425
B18	.014489	.83486	.83941	.84393	.84844	.85280	.85719	.86157	.86589	.87025	.87449	.87872	.88290	.88704
B19	.009284	.84621	.85099	.85579	.86055	.86506	.86970	.87430	.87886	.88344	.88788	.89232	.89672	.90098
B20	.006629	.85475	.85963	.86459	.86953	.87434	.87927	.88391	.88862	.89313	.89774	.90238	.90703	.91143
C1	.08524	.79022	.79431	.79789	.80125	.80490	.80833	.81175	.81512	.81854	.82192	.82524	.82855	.83184
C2	.05903	.79965	.80367	.80743	.81098	.81469	.81842	.82199	.82561	.82923	.83275	.83628	.83975	.84325
C3	.03767	.81078	.81504	.81908	.82277	.82677	.83072	.83450	.83841	.84224	.84601	.84971	.85346	.85710
C4	.018541	.82872	.83313	.83766	.84195	.84629	.85057	.85480	.85892	.86311	.86726	.87139	.87551	.87956
C5	.010837	.84253	.84733	.85199	.85666	.86122	.86582	.87031	.87485	.87931	.88373	.88814	.89248	.89679

the properties of the buffer anions alone, for it is impossible to obtain the activity-coefficient term at zero ratio of chloride to buffer and maintain, at the same time, a constant ratio of buffer to added salt. A series of measurements of solutions containing barium chloride was considered desirable, however, to aid in determining pK as accurately as possible.

Barium chloride, of reagent grade, was purified by recrystallization from water, powdered, and dried at 125° C. The emf data for phenolsulfonate buffers with added barium chloride are given in table 3.

TABLE 3.—*Electromotive forces of hydrogen–silver-chloride cells containing mixtures of potassium p-phenosulfonate* (m_1), *potassium sodium p-phenolate sulfonate* (m_2), *and barium chloride* (m_4)

[$m_2=0.9854m_1$; $m_4=0.5092m_1$]

Solution number	m_1	E_{0}°	E_{5}°	E_{10}°	E_{15}°	E_{20}°	E_{25}°	E_{30}°	E_{35}°	E_{40}°	E_{45}°	E_{50}°	E_{55}°	E_{60}°
D1	0.07950	0.79066	0.79435	0.79801	0.80128	0.80489	0.80844	0.81183	0.81518	0.81868	0.82198	0.82528	0.82864	0.83198
D2	.07455	.79223	.79596	.79964	.80303	.80665	.81018	.81366	.81702	.82053	.82390	.82724	.83059	.83390
D3	.05521	.79959	.80349	.80733	.81096	.81470	.81838	.82205	.82564	.82925	.83280	.83632	.83979	.84324
D4	.03890	.80821	.81229	.81632	.82022	.82412	.82801	.83188	.83566	.83951	.84325	.84696	.85072	.85428
D5	.03033	.81468	.81885	.82295	.82702	.83104	.83513	------	------	------	------	------	------	------
D6	.02901	.81556	.81979	.82394	.82802	.83203	.83606	.84008	.84399	.84793	.85183	.85569	.85951	.86326
D7	.018064	.82779	.83226	.83666	.84092	.84527	.84958	.85380	.85794	.86215	.86629	.87039	.87442	.87848
D8	.015583	.83163	.83621	.84073	.84509	.84948	.85381	.85816	.86253	.86659	.87080	.87495	.87911	.88319
D9	.012138	.83800	.84263	.84722	.85171	.85622	.86070	.86516	.86952	.87394	.87827	.88256	.88680	.89102
D10	.008828	.84626	.85110	.85590	.86054	.86523	.86983	.87449	.87901	.88350	.88798	.89242	.89683	.90104

4. Buffers with added trisodium citrate

In the search for a neutral salt that would yield trivalent ions, trisodium citrate was chosen. A preparation of the salt, of reagent grade, was crystallized from water and dried to constant weight at 130° C.

The pH change when small amounts of sodium hydroxide were added to a 0.05-m solution of trisodium citrate was determined with the use of thymol blue. The pH was found to increase from 8.4 to 9.0 upon the addition of 5×10^{-5} mole of the alkali to a liter of the citrate solution. Thus, m_1/m_2 for a 0.1-m phenolsulfonate buffer initially

TABLE 4.—*Electromotive forces of hydrogen–silver-chloride cells containing mixtures of potassium p-phenolsulfonate* (m_1), *potassium sodium p-phenolate sulfonate* (m_2), *sodium chloride* (m_3), *and trisodium citrate* (m_4).

[$m_2=0.9888m_1$; $m_3=0.9521m_1$; $m_4=0.3334m_1$]

Solution number	m_1	E_{0}°	E_{5}°	E_{10}°	E_{15}°	E_{20}°	E_{25}°	E_{30}°	E_{35}°	E_{40}°	E_{45}°	E_{50}°	E_{55}°	E_{60}°
E1	0.10611	0.78554	0.78897	0.79242	0.79582	0.79903	0.80267	0.80590	0.80855	0.81178	0.81523	0.81840	0.82145	0.82486
E2	.08339	.79134	.79498	.79855	.80209	.80549	.80904	.81243	.81591	.81930	.82263	.82596	.82927	.83257
E3	.07267	------	------	------	------	------	.81271	------	------	------	------	------	------	------
E4	.05579	.80101	.80487	.80867	.81236	.81598	.81991	.82363	.82726	.83085	.83441	.83795	.84147	.84496
E5	.04833	.80458	.80864	.81241	.81626	.81996	.82376	.82747	.83111	.83478	.83858	.84213	.84557	.84921
E6	.02841	.81779	.82208	.82628	.83042	.83441	.83856	.84270	.84666	.85062	.85460	.85852	.86239	.86618
E7	.02052	.82627	.83072	.83505	.83934	.84345	.84789	.85193	.85607	.86021	.86431	.86839	.87233	.87633
E8	.010988	.84187	.84670	.85136	.85608	.86049	.86526	.86971	.87421	.87871	.88317	.88749	.89175	.89601
E9	.007951	.85041	.85529	.86013	.86488	.86952	.87451	.87910	.88375	.88833	.89295	.89742	.90197	.90643
E10	.005326	------	------	------	------	------	.88558	------	------	------	------	------	------	------

TABLE 5.—*Electromotive forces of hydrogen–silver-chloride cells containing mixtures of potassium p-phenolsulfonate* (m_1), *potassium sodium p-phenolate sulfonate* (m_2), *with added neutral salt* (m_4), *and varying molalities of sodium chloride* (m_3)

Solution number	m_1	m_2	m_3	m_4 (KNO_3)	E_{0}°	E_{5}°	E_{10}°	E_{15}°	E_{20}°	E_{25}°	E_{30}°	E_{35}°
F1	0.04300	0.04309	0.02589	0.04310	0.81898	0.82314	0.82728	0.83168	0.83565	0.83951	0.84350	0.84737
F2	.04300	.04309	.016602	.04310	.82957	.83395	.83832	.84278	.84698	.85102	.85534	.85951
F3	.04300	.04309	.008233	.04310	.84599	.85071	.85544	.86020	.86473	.86914	.87359	.87802
				m_4 (Na_2SO_4)								
F4	.04300	.04309	.02557	.04310	.81869	.82280	.82699	.83130	.83531	.83921	.84328	.84724
F5	.04300	.04309	.015982	.04310	.82770	.83400	.83824	.84299	.84719	.85118	.85556	.85978
F6	.04300	.04309	.008634	.04310	.84410	.84880	.85342	.85824	.86270	.86712	.87161	.87609
F7	.04300	.04309	.008038	.04310	.84607	.85075	.85540	.86203	.86471	.86912	.87368	.87817
				m_4 ($Na_3C_6H_5O_7$)								
F8	.04300	.04309	.02510	.014367	------	------	.82791	.83223	.83630	.84025	.84443	.84848
F9	.04300	.04309	.016448	.014367	.82930	.83374	.83812	.84274	.84701	.85114	.85541	.85965
F10	.04300	.04309	.008340	.014367	.84547	.85019	.85486	.85964	.86420	.85863	.87312	.87770

at pH 9.0 could be changed only 0.1 percent by adding 0.05 mole of trisodium citrate to a liter of buffer. This change corresponds to 0.0004 in pH and pK, or 0.02 mv in emf. For the mixtures of series E, in which the ratio of molality of the trisodium citrate to that of each buffer salt was 0.33, the correction is even smaller.

The experimental data at 0° to 60° C for mixtures containing trisodium citrate are listed in table 4. The results for solutions containing potassium nitrate ($R=1$), sodium sulfate ($R=1$), and trisodium citrate ($R=0.33$), with varying ratios of sodium chloride to buffer, are given in table 5.

IV. Second Dissociation Constant of *p*-Phenolsulfonic Acid

Values of pK, the negative of the common logarithm of the second dissociation constant (that of the phenol group) of *p*-phenolsulfonic acid were derived from the measurements of the solutions in series A, B, C, D, and E by the method described in an earlier section. Figure 1 is a plot of the values of pK' at 25° C as a function of ionic strength for all five series. In table 6, the values of a^* that gave the best straight line for extrapolation and of β^*, the negative of the slope of this line, are listed for each series at each of the 13 temperatures.

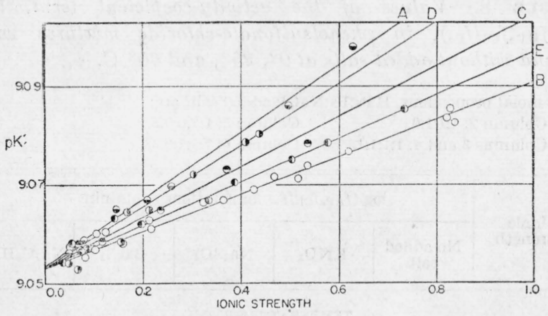

FIGURE 1.—*Plots of* pK' *as a function of ionic strength at 25° C.*

The letters indicate the series marking (tables 1 to 4) ◒=series A; ○=series B; ◓=series C; ◑=series D; ◐=series E.

TABLE 6.—*Values of a^* and β^* for five series of phenolsulfonate buffers at 0° to 60° C*

t	Series A, KNO_3		Series B, Na_2SO_4		Series C, Na_2SO_4		Series C, $BaCl_2$		Series E, $Na_3C_6H_5O_7$	
	a^*	$-\beta^*$	a^*	$-\beta^*$	a^*	$-\beta^*$	a^*	$-\beta^*$	a^*	$-\beta^*$
°*C*										
0	8.0	0.106	8.5	0.052	8.3	0.061	7.7	0.086	8.5	0.057
5	8.0	.100	8.5	.046	8.3	.066	7.7	.082	8.5	.054
10	8.0	.091	8.4	.046	8.2	.062	7.6	.080	8.4	.050
15	8.0	.087	8.4	.042	8.1	.051	7.6	.067	8.4	.045
20	8.0	.078	8.3	.039	8.1	.049	7.5	.070	8.3	.042
25	8.0	.072	8.2	.036	8.0	.051	7.5	.065	8.2	.044
30	8.0	.059	8.1	.037	8.0	.043	7.5	.060	8.2	.041
35	8.0	.052	8.0	.036	8.0	.043	7.5	.057	8.2	.036
40	8.0	.048	8.0	.034	8.0	.040	7.5	.057	8.2	.034
45	8.0	.046	8.0	.030	8.0	.039	7.5	.051	8.2	.030
50	8.0	.039	8.0	.027	8.0	.037	7.5	.049	8.2	.026
55	8.0	.040	8.0	.030	8.0	035	7.5	.049	8.2	.024
60	8.0	.032	8.0	.027	8.0	.032	7.5	.047	8.2	.022

The value of m_{OH} required for the hydrolysis correction was obtained conveniently from the emf data without the usual successive approximations by the relation [1]:

$$\log m_{OH} = (E - E^\circ)/k + \log m_{Cl} - pK_w, \quad (12)$$

where pK_w is the negative logarithm of the ionization constant of water. When m_{OH} was needed for buffers other than those for which emf data were available, it was computed from the approximation

$$m_{OH} \approx (K_w/K)/(m_1/m_2). \quad (13)$$

Values of K_w/K at 0° to 60° C are tabulated in the earlier paper [1]. Use of this approximate expression for m_{OH} introduces an error of about 0.002 unit in the pH of the 0.005-m phenolsulfonate buffer at 60° C. The error decreases rapidly as the temperature is lowered or the concentration of buffer is increased. The ionic strength, μ, and buffer ratio, m_{HPs}/m_{Ps}, are readily computed, with the aid of m_{OH}, by the equations

$$\mu = m_1 + 3m_2 + m_3 + nm_4 - m_{OH} \quad (14)$$

and

$$m_{HPs}/m_{Ps} = (m_1 + m_{OH})/(m_2 - m_{OH}). \quad (15)$$

The added salts were assumed to be completely ionized.[3]

A value of pK was computed from the emf measurement of each buffer solution at each temperature by eq 10 with the aid of a^* and β^* obtained by graphical means. The summary of pK (table 7) demonstrates the essential agree-

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[3] As the added salt (with the exception of barium chloride) takes no part in the cell reaction, an exact knowledge of its molality is unnecessary. If 5 percent of this added salt were undissociated, the change in ionic strength would be insufficient to alter log ($f_{HPs}f_{Cl}/f_{Ps}$) by 0.001, as can be shown with the aid of eq 9 or table 8. The value of n accordingly was assumed to be 1 for potassium nitrate, 3 for barium chloride and sodium sulfate, and 6 for trisodium citrate.

ment between the mean of the results of this investigation at each temperature with pK reported earlier [1]. The mean difference is less than 0.001 unit. At the higher temperatures, however, the deviations of each series from the mean are occasionally as large as 0.002 or 0.003. In general, the solutions containing potassium nitrate or barium chloride were found to yield lower values of pK than did those to which sodium sulfate or trisodium citrate had been added. In view of the acceptable agreement between the two measurements of pK, no recalculation of the thermodynamic constants for the dissociation of phenolsulfonate ion was made. Values of $E°*$ computed by eq 7 are given in the last column of the table.

Table 7.—*Summary of values of* pK *for the second dissociation of p-phenolsulfonic acid and* $E°*$ *at 0° to 60° C*

t	Series A, KNO_3	Series B, C, Na_2SO_4	Series D, $BaCl_2$	Series E, $Na_3C_6H_5O_7$	Mean	RP1559	$E°*$
° C							*Int. v*
0	9.3541	9.3528	9.3498	9.3524	9.352	9.352	0.74313
5	9.2856	9.2841	9.2818	9.2830	9.284	9.284	.74616
10	9.2203	9.2201	9.2187	9.2206	9.220	9.220	.74912
15	9.1606	9.1612	9.1593	9.1593	9.160	9.160	.75195
20	9.1038	9.1052	9.1033	9.1034	9.104	9.105	.75490
25	9.0527	9.0540	9.0514	9.0534	9.053	9.053	.75777
30	9.0052	9.0063	9.0038	9.0053	9.005	9.005	.76058
35	8.9585	8.9626	8.9591	8.9618	8.961	8.961	.76334
40	8.9190	8.9221	8.9176	8.9205	8.920	8.921	.76609
45	8.8805	8.8863	8.8811	8.8849	8.883	8.883	.76883
50	8.8480	8.8520	8.8472	8.8511	8.850	8.849	.77161
55	8.8144	8.8183	8.8143	8.8195	8.817	8.816	.77423
60	8.7868	8.7888	8.7845	8.7884	8.787	8.787	.77683

V. Effect of Neutral Salts on the Activity Coefficients

With the aid of a^* and β^* from table 6, a calculation of $\log (f_{HPs}f_{Cl}/f_{Ps})$ was made by eq 9, in order to compare the values of this term at several ionic strengths and at temperatures of 0°, 25°, and 60° C. The results are shown in table 8, where data for phenolsulfonate-chloride solutions without added salt are also given. For the latter, a^* is 8.0, and β^* at 0°, 25°, and 60° C has the values -0.079, -0.057, and -0.038 [4].

The change of the activity-coefficient term with the addition of neutral salt when the ionic strength remains unaltered is small, particularly at 25° C and higher temperatures.[4] In these concentrations, therefore, the added salts probably effect no large change in the electrostatic character of the buffer medium. The small effect of salt is evident in figure 2, where the activity-coefficient term and $(E-E°)/k+\log(m_{HPs}m_{Cl}/m_{Ps})$ are plotted as a function of the square root of the ionic strength.

Table 8.—*Values of the activity-coefficient term,* $\log (f_{HPs}f_{Cl}/f_{Ps})$*, in phenolsulfonate-chloride mixtures with and without added salts at 0°, 25°, and 60° C.*

The molal proportions, HPs:Ps:NaCl: added salt, are:
Column 2; 1:1:1:0.
Columns 3 and 4; 1:1:1:1.
Column 5; 1:1:0:0.5.
Column 6; 1:1:1:0.33.

Ionic strength	$\log (f_{HPs}f_{Cl}/f_{Ps})$ for solutions containing—				
	No added salt	KNO_3	Na_2SO_4	$BaCl_2$	$Na_3C_6H_5O_7$
TEMPERATURE 0° C					
0.02	0.099	0.099	0.098	0.100	0.098
.05	.134	.133	.133	.136	.132
.1	.162	.159	.160	.164	.159
.2	.186	.181	.185	.189	.184
.3	.197	.189	.198	.200	.196
.5	.204	.191	.208	.207	.206
.6	.204	.188	.210	.206	.207
TEMPERATURE 25° C					
0.02	0.104	0.104	0.104	0.105	0.103
.05	.140	.140	.140	.143	.140
.1	.170	.169	.170	.174	.169
.2	.198	.195	.199	.203	.198
.3	.211	.207	.213	.218	.212
.5	.223	.216	.230	.230	.226
.6	.225	.217	.234	.232	.229
TEMPERATURE 60° C					
0.02	0.111	0.111	0.111	0.112	0.110
.05	.150	.150	.150	.153	.149
.1	.182	.183	.183	.187	.182
.2	.214	.215	.216	.219	.214
.3	.230	.232	.233	.236	.231
.5	.247	.250	.252	.253	.250
.6	.251	.255	.258	.258	.256

1. Buffer Solutions Without Added Salt

A determination of the effect of a changing ratio of sodium chloride on a^* and β^* was reported earlier [4]. As in the present work, the 1:1 phenolsulfonate buffer was studied by means of emf measurements at 0° to 60° C. The value of

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[4] Nims [6] has determined $-\log (f_{Cl}f_{HG}/f_{G})$, where G represents the singly charged glycolate anion, in glycolate buffer solutions containing chloride and has found a pronounced salt effect. Three series of solutions, in which the cation was respectively potassium, lithium, and barium, gave quite different values for the activity-coefficient term.

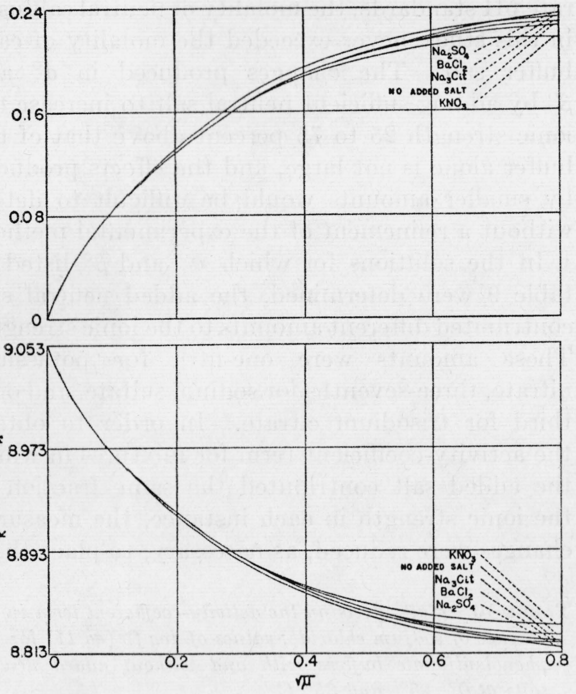

FIGURE 2.—*Salt effect on the activity-coefficient term (upper-curve) and on* $(E-E^{\circ})/k+\log(m_{HP}m_{Cl}/m_{Ps})$ *(lower curve) at 25° C. Compare eq 9 and 10.*

a^* was found to be 8.0 A at all temperatures and to be substantially unchanged when the molal ratio of sodium chloride to each buffer salt was reduced from unity to one-tenth. The parameter β^* was negative and changed in a regular manner as the temperature was increased.

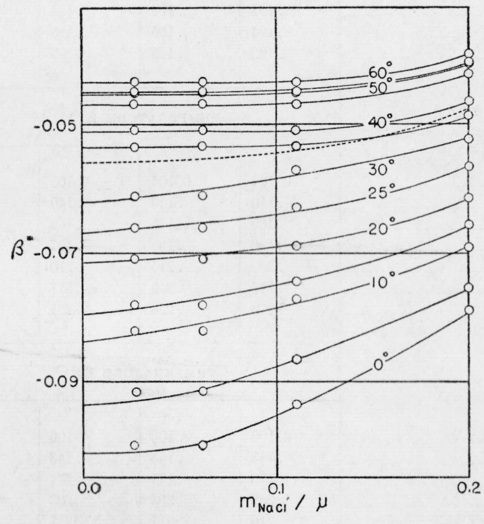

FIGURE 3.—*Plots of β^* as a function of m_{NaCl}/μ for 1:1 phenolsulfonate buffers with varying amounts of sodium chloride.*

Figure 3 shows the change of β^* with the ratio of sodium chloride to buffer salt. The limiting values, β°, are given in table 9. The value of a° is 8.0 A at each temperature.

TABLE 9.—*Values of a° and β° for 1:1 phenolsulfonate buffers without added salt and for buffers containing potassium nitrate, sodium sulfate and trisodium citrate (molality of added neutral salt)/(molality of each buffer salt)=1 (KNO_3); 1(Na_2SO_4); and 1/3($Na_3C_6H_5O_7$).*

t	Without added salt		KNO_3		Na_2SO_4		$Na_3C_6H_5O_7$	
	a°	β°	a°	β°	a°	β°	a°	β°
°*C*								
0	8.0	−0.101	8.0	−0.098	8.5	−0.046	8.5	−0.058
5	8.0	−.094	8.0	−.087	8.5	−.046	8.5	−.058
10	8.0	−.085	8.0	−.078	8.4	−.046	8.4	−.058
15	8.0	−.080	8.0	−.070	8.4	−.046	8.4	−.058
20	8.0	−.072	8.0	−.063	8.3	−.046	8.3	−.058
25	8.0	−.066	8.0	−.058	8.2	−.046	8.2	−.058
30	8.0	−.063	8.0	−.052	8.1	−.046	8.2	−.058
35	8.0	−.053	8.0	−.048	8.0	−.046	8.2	−.058
40	8.0	−.051	-----	-----	-----	-----	-----	-----
45	8.0	−.047	-----	-----	-----	-----	-----	-----
50	8.0	−.045	-----	-----	-----	-----	-----	-----
55	8.0	−.045	-----	-----	-----	-----	-----	-----
60	8.0	−.043	-----	-----	-----	-----	-----	-----

2. Buffer Solutions With Added Salt

The interdependence of a^* and β^* is noteworthy.[5] It is ordinarily difficult, in view of the normal experimental error of a series of points, to establish the correct value of a^* within 0.1 to 0.2 A by choice of the value that yields the best straight line. An error of this magnitude in a^* is, fortunately, offset almost completely by a compensatory change in β^*. For example, if 8.2 A were chosen for a^*, instead of 8.0 A, in the mixtures with varying amounts of sodium chloride but without added neutral salt, the plot of β^* at 25° C with respect to the fractional contribution of sodium chloride to the ionic strength would follow the dashed line of figure 3, and β° would be assigned a value of −0.056 instead of −0.066. With the use of $a^{\circ}=8.2$ and $\beta^{\circ}=-0.056$, $\log f^{\circ}_{R}$ for the 0.1-*m* buffer (ionic strength of 0.4) calculated from eq 11 would be 0.2157 instead of 0.2154 at 25° C, and at an ionic strength of 0.01, the difference would be 0.0006.

Advantage was taken of this agreement in

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[5] Van Rysselberghe and Eisenberg [7] and Robinson and Harned [8] have suggested modifications of the Hückel equation, in which a single parameter expresses successfully the activity coefficient of the alkali halides and hydrogen halides up to concentrations of 1 to 4 *m*.

determining the limiting parameters for buffers that contained neutral salt in the absence of sodium chloride. For the complete analysis of the data of series F given in table 5, it was not necessary to have an independent measure of a^* for each ratio of sodium chloride to buffer and neutral salt. Such a determination would require the study of several dilutions of each mixture of series F. Instead, a^* for the appropriate mixture of buffer and salt was selected from table 6, pK' was computed for each solution at each temperature, and β^* was evaluated from the relation,

$$\beta^* = (\mathrm{p}K - \mathrm{p}K')/\mu. \tag{16}$$

Plots of β^* as a function of m_{NaCl}/μ were constructed, and $\beta°$, the intercept for zero concentration of sodium chloride, was found. Five experimental points determined the extrapolation for solutions that contained sodium sulfate, whereas measurements that represented four different ratios of sodium chloride to buffer were available for solutions with potassium nitrate and trisodium citrate. The limiting parameters for the mixtures containing neutral salt are given in table 9, together with those for the 1:1 buffer without added salt. The data for solutions with varying contents of sodium chloride did not extend above 35° C. The parameter $\beta°$ has constant values of -0.046 and -0.058, within 0.004, for the mixtures with sodium sulfate and trisodium citrate, respectively, in this range of temperatures. The limiting values of β^* are thought to be correct to ± 0.006. This uncertainty corresponds to an error of 0.003 in the activity-coefficient term at an ionic strength of 0.5.

It is now possible, with eq 11 and the constants given in table 9, to compute $\log f_R^\circ$ for 1:1 phenolsulfonate buffers that contain potassium nitrate or sodium sulfate in molalities equal to that of each buffer salt, or trisodium citrate in one-third the molality of the buffer. Furthermore, the value of this activity-coefficient term is likewise known for the same buffer in the absence of salt. The change which results from adding a single definite amount of each of three neutral salts of different valence types to a 1:1 phenolsulfonate buffer has therefore been determined, but the effect of other concentrations of salt, larger or smaller than this one, is still unknown. Inasmuch as the effect on the pH of relatively small amounts of salt is of most concern in the preparation and use of accurate pH standards, the molality of neutral salt used in this study never exceeded the molality of each buffer salt. The changes produced in $a°$ and $\beta°$ by adding sufficient neutral salt to increase the ionic strength 25 to 75 percent above that of the buffer alone is not large, and the effects produced by smaller amounts would be difficult to detect without a refinement of the experimental method.

In the solutions for which $a°$ and $\beta°$ listed in table 9 were determined, the added neutral salt contributed different amounts to the ionic strength. These amounts were one-fifth for potassium nitrate, three-sevenths for sodium sulfate, and one-third for trisodium citrate. In order to obtain the activity-coefficient term for mixtures in which the added salt contributed the same fraction of the ionic strength in each instance, the measured changes were reduced, as necessary, to place them

TABLE 10.—*Salt effects on the activity-coefficient term in the absence of sodium chloride; values of log f_R° (eq 11) for 1:1 phenolsulfonate buffers with and without added neutral salts at 0°, 25°, and 35° C*

The added salts contribute one-fifth of the inoic strength in each case.

Ionic strength	log f_R° for buffer solutions containing—			
	No added salt	KNO_3	Na_2SO_4	$Na_3C_6H_5O_7$
	TEMPERATURE 0°C			
0 02	0.099	0.099	0.098	0.098
.05	.133	.133	.133	.132
.1	.160	.160	.160	.159
.2	.182	.183	.183	.183
.3	.191	.192	.194	.193
.4	.194	.195	.198	.198
.5	.193	.195	.199	.199
	TEMPERATURE 25°C			
.02	0.104	0.104	0.103	0.103
.05	.140	.140	.140	.139
.1	.169	.170	.169	.168
.2	.196	,198	.197	.195
.3	.209	.211	.210	.208
.4	.215	.219	.217	.215
.5	.219	.223	.221	.219
	TEMPERATURE 35°C			
.02	0.106	0.106	0.106	0.105
.05	.143	.143	.143	.142
.1	.173	.174	.174	.172
.2	.202	.203	.203	.200
.3	.216	.217	.217	.214
.4	.224	.226	.225	.221
.5	.229	.231	.230	.225

on a common basis, in direct proportion to the fractional contribution of the salt to the ionic strength. The largest of the measured salt effects was 0.018, found when sodium sulfate ($R=1$) was present at 0° C and an ionic strength of 0.5. In view of the relatively small effects involved, this procedure for computing the effect of amounts of salt smaller than those actually used was considered justifiable.[6] A comparison of log f_R° for solutions in which the added salt makes up one-fifth of the total ionic strength is given in table 10.

No specific effects larger than the uncertainty of measurement are apparent in the data of table 10. The effectiveness of salts of the 1–1, 1–2, and 1–3 valence types at equal ionic strengths in altering the activity coefficients is nearly the same, and no marked abnormal influence of the increased ionic charge is evident. Furthermore, the salt effect of each of the three salts is no larger than the combined uncertainties inherent in the determination of β° and in the experimental measurements, or 0.006 at an ionic strength of 0.5. Changes larger than the estimated limits of error are found, as expected, for mixtures in which sodium sulfate and trisodium citrate contribute more than one-fifth of the ionic strength.

If, indeed, the change of log f_R° with addition of neutral salt approximates in character the behavior of log $(f_{\text{HPs}}/f_{\text{Ps}})$, it can be concluded that the effect of neutral salts in moderate concentrations on the pH of phenolsulfonate buffer solutions is governed primarily by the increase in ionic strength and not by the specific nature of the salt itself. When the added salt makes up one-fifth or less of the ionic strength, the pH of the solution is close to that of a solution of the pure buffer of the same total ionic strength.[7]

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[6] By analogy with mixtures of strong electrolytes, log f_R° at a given ionic strength is expected to vary in an approximately linear manner with change of composition, provided that the contribution of the salt to the ionic strength of the mixture is plotted. For a review of this topic, see chapter 15 of the monograph by Harned and Owen [9].

[7] Evidently the effect of salts on the negative of the common logarithm of the activity of hydrogen ion will be quite different from the change produced in $-\log m_{\text{H}}$ or $-\log c_{\text{H}}$, often considered to measure the salt effect on the pH (see, for example, reference 10). In general, addition of salt to a dilute solution of a weak acid causes m_{H} to increase and f_{H} to decrease. Hence, the product of these two quantities, the activity, may change less than does the concentration alone.

VI. References

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