

POTENTIOMETRIC DETERMINATION OF THE
AUTOPROTOLYSIS CONSTANT OF N-BUTANOL

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The autoprotolysis constant of n-
butanol is determined at 25° potenti-
metrically with the aid of the two cells:
Glass electrode | HCl(m), BuOH || ZnCl₂(sat.), BuOH,
Hg₂Cl₂, Hg
and

Glass electrode | KOH(m), BuOH || ZnCl₂(sat.), BuOH,
Hg₂Cl₂, Hg

The mean activity coefficients (γ_{\pm}) of
hydrogen chloride in n-butanol are com-
pared to the corresponding theoretical
values.

The study of the ion-solvent interaction is quite im-
portant to account for acid-base equilibria in aqueous and
non-aqueous solvents. For such study, the evaluation of the
autoprotolysis constant of the solvent and the activity co-
efficient of the strong electrolytes dissolved in is an es-
sential prerequisite.

Determination of the autoprotolysis constants of solv-
ents and accordingly their pH scales, is important for app-
lication of these solvents in acid-base titrations. Evident-
ly, the weaker the self ionization of the solvent, the wider
the range of acid strength that might be studied in.

In continuation of the previous work on n-butanol and
its application as a solvent for weak acids¹, the present
study is devoted for the determination of the autoprotolysis
constant of this solvent. Further study of strong electro-
lyte-butanol interaction is also presented making use of

the experimentally found and theoretically deduced values of the activity coefficient of hydrogen chloride in n-butanol.

EXPERIMENTAL

Instrumentation: A titri-pH-meter (type OP 401/2 Radelkis Budapest) was used. The glass electrode was kept in n-butanol between E.M.F. measurements. The calomel electrode was filled with a saturated solution of zinc chloride in n-butanol. All measurements were carried out at $25 \pm 0.5^\circ$ while protecting the solution with nitrogen gas.

Reagents: Chemicals used were all of analytical grade. Twice distilled water was used in the preparation of aqueous solutions. n-Butanol was purified as described previously¹.

Sodium Carbonate Solutions, 0.05 and 0.005 N: Prepared by solving the accurately weighed amount of the anhydrous salt in twice distilled water.

The HCl + n-BuOH Stock Solution: $m_{\text{HCl}} = 0.25 \text{ mol/kg}$: Prepared by dissolving HCl gas in n-BuOH. Dry HCl gas was produced by the reaction of H_2SO_4 and NH_4Cl . The HCl concentration was determined potentiometrically by titration with potassium hydroxide solution.

Perchloric Acid, 0.02 N: Prepared by adding 1.7 ml of 72% perchloric acid to 1 L of ethanol and standardization with sodium carbonate.

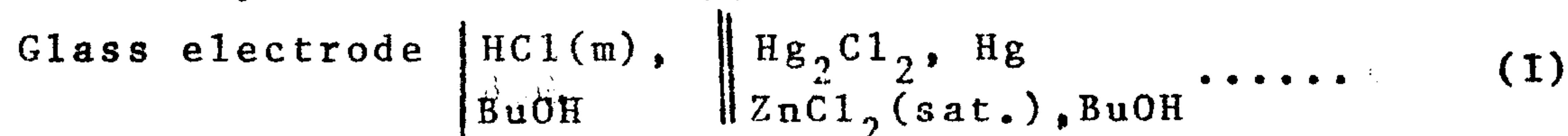
The KOH + n-BuOH Stock Solution, $m_{\text{KOH}} = 0.025 \text{ mol/kg}$: Prepared by dissolving the required amount of KOH pellets in small volume of n-butanol in the absence of air. The solution was diluted with additional n-BuOH and standardized against HClO_4 .

RESULTS AND DISCUSSION

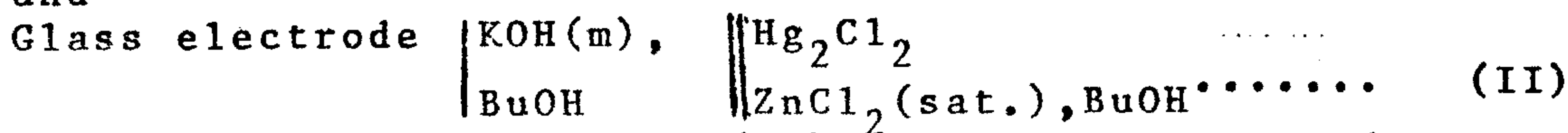
According to Brønsted-Lowery assumptions^{2,3}, the strongest acid in a solvent is its protonated form, lyonium ion, and the strongest base is the deprotonated form, lyate ion. Thus, the strongest acid existing in n-butanol (BuOH)

is the (BuOH_2^+) ion and the strongest base is the anionic conjugate base of the solvent (BuO^-) . In the present study hydrogen chloride was taken to afford the (BuOH_2^+) ion while potassium hydroxide was the precursor of the (BuO^-) ions.

The autoprotolysis constant of n-butanol was thus determined potentiometrically, using the following cells:



and



The E.M.F. of the cell (II) may be represented by:
 $E = E_o + 0.059 \log a_{\text{SH}^+} = E_o + 0.059 \log K_s - 0.059 \log a_{\text{S}^-}$ (Eq 1)
 Where SH^+ and S^- stand for (BuOH_2^+) and (BuO^-) respectively.

It is possible to deduce the standard potential of cell (II) by studying the variation of E.M.F. of cell (I) with the concentrations of hydrogen chloride in n-butanol and calculating the values of E_o' :

$$E_o' = E - 0.059 \log m_{\text{HCl}} = E_o + 0.059 \log \gamma_{\text{HCl}} \dots\dots\dots \text{(Eq 2)}$$

The plot of E_o' against \sqrt{m} was linear and gave E_o at $m = 0$. The value obtained is 0.468 v.

The same result was also obtained by applying (Eq 3) and extrapolation of the E_o'' vs. \sqrt{m} plot to $m = 0$.

$$E_o'' = E - 0.059 \log m_{\text{HCl}} + Az_i^2 \sqrt{I} \dots\dots\dots \text{(Eq 3)}^5$$

where A in n-butanol = $4.324 A^0$, z_i is the charge of ions, and I is the ionic strength of the solution.

According to (Eq 4) the extrapolation of E_o'' vs. \sqrt{m} plot to $m = 0$, gives an intercept of 0.468 V.

$$E_o'' = E - 0.059 \log m \alpha_{(\text{HCl})} \dots\dots\dots \text{(Eq 4)}$$

The degree of ionization of hydrogen chloride in n-butanol (α) is given by the relation:

$$K_a = \frac{m \alpha^2}{1 - \alpha} \dots\dots\dots \text{(Eq 5)}$$

where k_a is the dissociation constant of hydrogen chloride in n-butanol ($K_a = 1.32 \times 10^{-3}$), m and γ_{\pm} are the molality and the mean coefficient activity of hydrogen chloride in

n-butanol respectively (Table 1).

Application of the standard potential (E_o) and the measured E.M.F. values of cell (II) at different molalities of potassium hydroxide (m) in (Eq 6) afforded several values of pK'_s (Table 2).

$$pK'_s = pK_s + \log m_{KOH} = \frac{E_o - E}{0.059} - \log m_{KOH} \dots\dots (Eq 6)$$

The apparent autoprotolysis constant of n-butanol (pK'_s) could be determined by extrapolation of pK'_s vs. \sqrt{I} plot to $m = 0$. The pK^*_s value was 19.45.

The more accurate pK^{**}_s value (19.83) was obtained by extrapolation of the pK_s vs. \sqrt{m} to $m = 0$ (Eq 7).

$$pK^{**}_s = \frac{E_o - E}{0.059} - \log m \alpha (KOH) \dots\dots\dots (Eq 7)$$

where α is the degree of ionization of potassium hydroxide in n-butanol at molality (m). The different values of α were derived from (Eq 9) using the mean activity coefficient of potassium hydroxide (γ_{KOH}). The latter can be evaluated using the relation:

$$pK'_s - pK^*_s = \log \gamma_{KOH} \dots\dots\dots (Eq 8)$$

$$K_b(KOH) = \frac{m \alpha^2 \gamma^2}{1 - \alpha} \dots\dots\dots (Eq 9)$$

For application of (Eq 9), a value of 1.17×10^{-4} was taken for $K_b(KOH)$ in n-butanol, which was potentiometrically determined in the current work.

Finally (Eq 10) was applied for the determination of the absolute value of the autoprotolysis constant of n-butanol.

$$pK_s = \frac{E_o - E}{0.059} - \log m \alpha \gamma (KOH) \dots\dots\dots (Eq 10)$$

The value found was 19.83 in excellent accordance with that obtained by the extrapolation method (Eq 7).

The considerably small value of the autoprotolysis constant of n-butanol can evidently reflect the large pK-scale within which many acids and bases can be titrated and differentiated. This finding also goes with the

relatively low differentiating properties of methanol and ethanol which possess relatively higher autoprotolysis constants⁶. Such a consideration can be concluded, also from the order of the dielectric constant values of these alcohols (Table 3).

The second part of this work considered determination of the mean activity coefficient of hydrogen chloride ions (γ_{\pm}) in n-butanol. This was thought essential as it might provide a useful insight into the phenomena of ion-solvent interaction.

When the activity coefficient values were determined using various increasing concentrations of hydrogen chloride in n-butanol, the anticipated decrease in γ_{\pm} values was found not so distinct (Table 1).

Comparison of these values with those obtained for the corresponding concentrations of hydrogen chloride in ethanol and methanol (Table 4) leads to the assumption, that the dissociation of hydrogen chloride increases when descending the alcohol series, being maximum in water.

In alignment with the self-ionization capabilities of the alcohols listed, as determined by their autoprotolysis constants, no appreciable decrease in the dissociation process of hydrogen chloride was observed on passing from ethanol to n-butanol.

This behaviour can be attributed to the relatively non-appreciable differences between the thermodynamic and/or kinetic stabilities of the ethyl and n-butyl moieties during self-ionization or protonation of the corresponding alcohol.

When the simple and extended Debye-Hückel equations⁷ were applied to calculate the theoretical γ_{\pm} values for different concentrations of hydrogen chloride in n-butanol (Table 5) a considerable deviation from the experimentally determined γ_{\pm} values was noticed (Fig I). However, this deviation was found negligible for concentrations of 0.001m HCl in n-BuOH.

Evidently, for a better and representative consideration of the electrolyte-solvent interaction, γ_{\pm} values should be determined experimentally. For the Debye-Hückel equation and its extension, the validity of the A, a and B parameters is generally doubtful, since an approximation is allowed for by neglecting variations in these parameters that can take place at strong solvent-electrolyte interactions⁷.

Table 1- Determination Of The Standard Potential of Cell (1)

m_{HCl}	$\frac{m_{HCl}}{4}$	-E	$-E_o'$	$\beta \pm$	α	$-E_o''$	$-E_o'''$
0.0010	0.032	0.288	0.465	0.870	0.693	0.473	0.475
0.0021	0.046	0.305	0.463	0.810	0.580	0.474	0.479
0.0044	0.066	0.322	0.461	0.761	0.477	0.478	0.482
0.0082	0.090	0.336	0.459	0.690	0.400	0.483	0.485
0.0141	0.119	0.346	0.455	0.600	0.348	0.489	0.486
0.0265	0.163	0.358	0.451	0.510	0.298	0.499	0.487
0.0510	0.226	0.369	0.445	0.410	0.263	0.513	0.485
0.1020	0.320	0.381	0.440	0.332	0.250	0.521	0.480
0.2200	0.467	0.395	0.434	0.260	0.262	0.548	0.467

Potentiometric Determination Of The
Autoprotolysis Constant Of N-Butanol

Table 2- Determination Of The Autoprotolysis Constant Of n-Butanol

m_{KOH}	$\frac{1}{2} m_{KOH}$	E	pK'_s	β_{\pm}	α	pK''_s	pK'''_s
0.0015	0.038	0.495	19.15	0.501	0.430	19.52	19.83
0.0031	0.056	0.506	19.01	0.372	0.403	19.41	19.83
0.0063	0.079	0.514	18.85	0.251	0.420	19.23	19.83
0.0127	0.113	0.514	18.54	0.135	0.504	18.84	19.71
0.0246	0.157	0.514	18.25	0.063	0.650	18.44	19.64

Table 3 - The Autoprotolysis Constants and Dielectric Constants of
Certain Alcohols.

Solvent *	Methanol	Ethanol	n-Butanol
pK_s	: 16.7	19.1	19.8
DE	: 32.7	25.2	17.5

Reference (6)

Table 4-- The Activity Coefficient, γ_{\pm} , of HCl in Different Solvents

m_{HCl}	$\sqrt{m_{HCl}}$	water*	Methanol*	Ethanol*	n-Butanol
0.001	0.032	0.984	0.339	0.898	0.872
0.002	0.046	0.971	0.804	0.778	0.810
0.005	0.071	0.947	0.744	0.728	0.720
0.010	0.100	0.924	0.700	0.632	0.650
0.020	0.141	0.894	0.625	0.562	0.520
0.051	0.226	0.860	0.514	0.426	0.410
0.102	0.320	0.810	0.440	0.352	0.332
0.200	0.447	0.783	0.344	0.286	0.276

* Reference (5), P. 556.

Table 5- The Relation Between Experimental Mean Activity Coefficient Of HCl in n-Butanol and Calculated from Debye-Huckel Equation

m_{HCl}	Experimental		Limit, D-H @		Extend. D-H I		Extend. D-H II	
	γ	$-108\gamma'$	γ	$-108\gamma'$	γ	$-108\gamma'$	γ	$-108\gamma'$
0.0010	0.032	0.872	0.060	0.729	0.137	0.737	0.133	0.752
0.0021	0.046	0.810	0.092	0.633	0.199	0.645	0.190	0.672
0.0044	0.066	0.761	0.119	0.518	0.285	0.540	0.268	0.583
0.0082	0.090	0.690	0.161	0.407	0.391	0.438	0.358	0.500
0.0141	0.119	0.600	0.222	0.307	0.513	0.348	0.459	0.428
0.0265	0.163	0.510	0.292	0.198	0.704	0.248	0.605	0.349
0.0510	0.226	0.410	0.387	0.106	0.976	0.160	0.796	0.276
0.1020	0.320	0.332	0.479	0.045	1.382	0.090	1.048	0.213
0.2200	0.467	0.260	0.585	0.010	2.020	0.042	1.377	0.161

$-\log \gamma = AZ_1^2 I^{\frac{1}{2}}$, where A in n-butanol = 4.324 A°

$I - \log \gamma = AZ_1^2 I^{\frac{1}{2}}$

$\frac{1 + aB/I}{1 + aB/I}$, where aB = 1

$I - \log \gamma = \frac{AZ_1^2 I^{\frac{1}{2}}}{1 + aB/I}$

where a = 5.3 A° and B in n-butanol = 0.6243x10⁸ A°

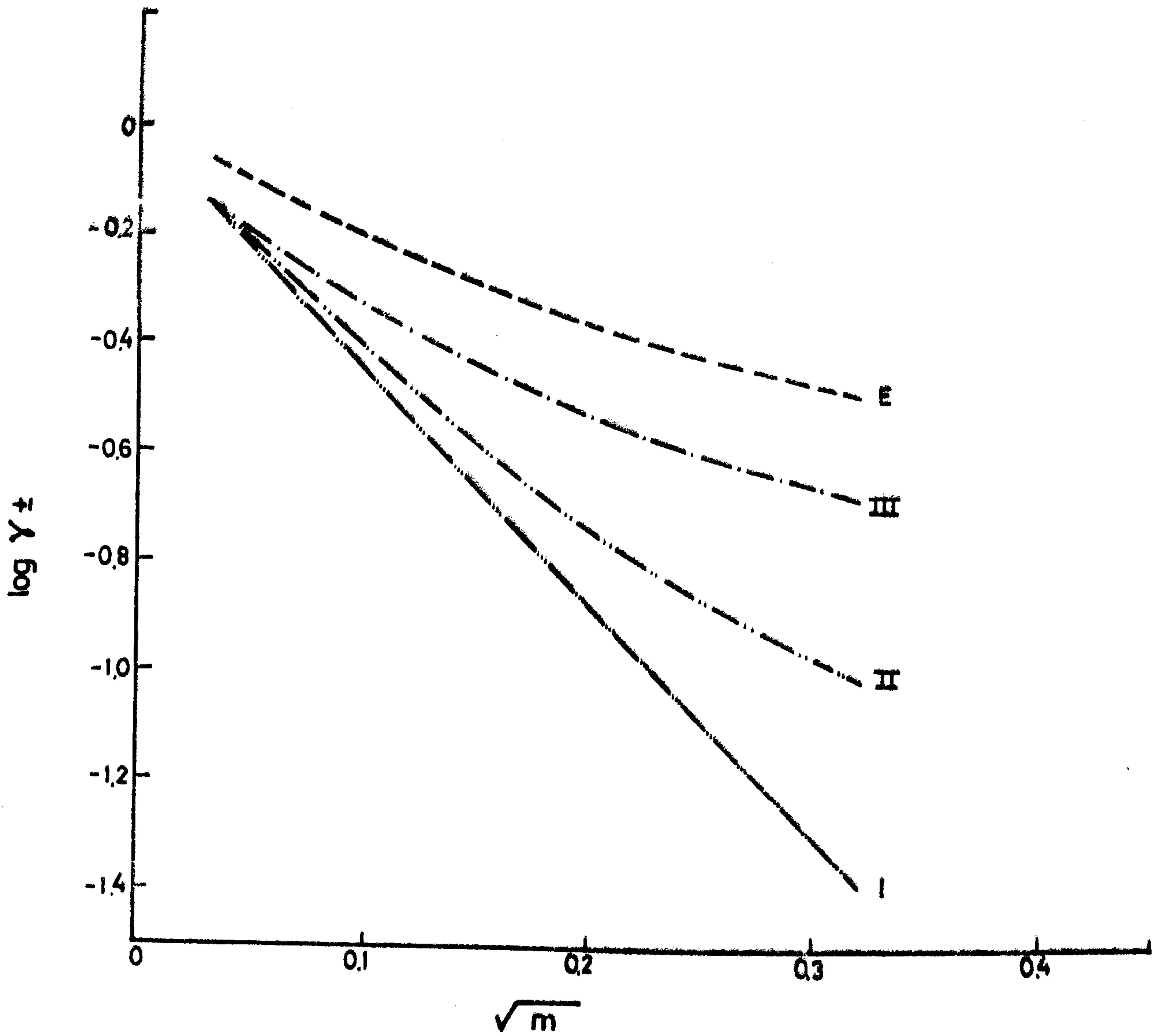


Fig. I. Relation Between Experimental and Calculated $\log \gamma_{\pm}$ HCl in n-Butanol.

Key: Experimental (E) ; Simple (I) ; Extended (II and III) Debye-Hückel Equation.

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تعيين ثابت تأين الكحول البيوتيلي

نوال على الرباط

قسم الكيمياء الصيدلية - كلية الصيدلة - جامعة اسبوط

باستخدام طرق قياس فرق الجهد لخلية كهربائية مكونة من قطبين احدهما القطب الزجاجي والاخر الكالوميل امكن تعيين ثابت تأين الكحول البيوتيلي وجد ان سالب هذا التاين يكافى ١٩٨ وحدة.

تضمن البحث كذلك تعيين ثابت فرق جهد الخلية المستخدمة عند ٢٥ م - تم تعيين درجة تاين ومعامل نشاط ايونات كلوريد الهيدروجين وهيدروكسيد البوتاسيوم بنفس المذيب ومقارنة النتائج الحالية بما يماثلها في الماء والكحول الايثيلي والميثيلي وجد ان ثابت تأين الكحول البيوتيلي وتبعاً له درجة تأين كلوريد الهيدروجين في وسطه قد انخفضا عن مثيلاتها في الكحولين المذكورين والماء.

لكن درجة الانخفاض بالنسبة للكحول الايثيلي تبدو اقل من المتوقع مما يجعلنا نعتقد ان الخواص الديناميكية الكهربائية بشطري هذه الكحولين لا تختلف عن بعضهما كثيراً.

وبالتقدير الحسابي لمعامل تأين كلوريد الهيدروجين بنظرية ديبي وهيكسل وامتدادها وجد انه يختلف عن ذلك الذي تم تعيينه عملياً خصوصاً في التراكيز العالية لكلوريد الهيدروجين في الكحول البيوتيلي مما يؤكد احتياج هذه المعادلات لدالات تعكس تأثير التفاعلات التي تتم بين المذيب والمادة المذابة.

من ثم فالنتائج التي توصلنا اليها من خلال هذا البحث تشجعنا على بحث امكان تعيين المركبات الصيدلية ذات الخاصية القاعدية منفردة وفي مخاليطها وذلك بعد تعيين ثوابت تأينها في وسط هذا المذيب.