ADSORPTION OF *tert*-BUTYL ALCOHOL AT THE Hg|AQUEOUS PERCHLORATE INTERFACE IN THE PRESENCE OF TETRAMETHYLTHIOUREA

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The electrosorption behavior of *tert*-butyl alcohol at the mercury|aqueous $NaClO_4$–tetramethylthiourea was determined by a double layer differential capacity measurement. Adsorption of *tert*-butyl alcohol was analyzed using the constants obtained from the modified Flory–Huggins and virial isotherm. An increase in the relative surface excess for *tert*-butyl alcohol with increasing $NaClO_4$ concentration in the range from 0.1 to 1.0 M was confirmed. The observed effect may be the result of the weakest repulsive interaction between adsorbed *tert*-butyl alcohol molecules in 1.0 M $NaClO_4$ with 0.05 M tetramethylthiourea.
Keywords: Differential capacity; Adsorption isotherm; Electrostatic parameters; *tert*-Butyl alcohol; Tetramethylthiourea; Mercury electrode; Electrosorption; Electrochemistry.

The adsorption of organic sulfur compounds has been widely investigated[1–3]. Many of these compounds act as corrosion inhibitors[4–7]. Corrosion inhibitor mixtures are often used to improve their efficiency resulting in synergistic effects; however, an antagonistic effect is also possible[8]. Given the adsorption experimental data on surface-active substances on different metals, it appears that a similar mechanism of the formation of mixed adsorption layers on mercury operates. In general, the adsorption of neutral organic compounds from aqueous solutions on electrodes should be considered as a competitive process between the adsorbate and the solvent. In the case of two different organic substances, a problem of competitiveness also applies to these substances.

The work presented herein concerns studies of mixed adsorption layers formed by tetramethylthiourea (TMTU) and *tert*-butyl alcohol (TB). The for-

mer substance undergoes chemisorption on a mercury electrode, however, the latter adsorbs physically. In addition, the paper describes the influence of the concentration of base electrolyte (0.1–1.0 M NaClO$_4$) on the properties of mixed adsorption layers. Our previous studies on adsorption on a mercury electrode in 1.0, 0.5 and 0.1 M NaClO$_4$ indicated the strongest adsorption of both TMTU and TB in 1.0 M NaClO$_4$ [9–11]. These results confirm that in the adsorption of organic substances, displacement of water from the electrode surface is more difficult than the displacement of ClO$_4^-$ ions. The results presented earlier can be an input for a discussion concerning mixed adsorption layers formed by TMTU and TB. The homogeneity and purity of mercury surface provide excellent reproducibility of adsorption phenomena.

EXPERIMENTAL

Reagents

Analytical grade TMTU, TB and NaClO$_4$ (Fluka) were used without further purification. Water and mercury were double-distilled before use. *tert*-Butyl alcohol solutions in water were 0.01–0.5 M and TMTU solutions 0.05 M. The maximum concentration of TMTU was limited by its solubility. The solutions were deaerated by passing high-purity nitrogen over the solutions during the measurements at 298 ± 0.1 K. No corrections on the effect of the medium on the activity of the supporting electrolyte[12,13] and activity coefficients of the adsorbate[14] were made. The paper is a part of complex studies of the influence of the mixed adsorption layer on the kinetics of metal cations electroreduction. The NaClO$_4$ solutions at pH 3 were used in these studies to protect the hydrolysis of metal cations.

Apparatus

The experiments were performed in a three-electrode system with a dropping mercury electrode as a working electrode, an Ag|AgCl reference electrode, and a platinum spiral as a counter-electrode. A controlled-growth mercury drop electrode (CGMDE; MTM, Poland) was used. The differential capacity, C, of the double layer was measured with an Autolab frequency response analyzer (Eco Chemie, Netherlands) using the AC impedance technique. The reproducibility of the average capacity measurements was ±0.5%. The measurements were carried out at several frequencies in the range from 400 to 2000 Hz, with an amplitude of 5 mV. The equilibrium capacities were obtained by extrapolation to zero frequency of the dependence of the measured capacity on the square root of frequency. The potential of zero charge, E_z, was measured using a streaming electrode[15]. The interfacial tension, γ_z, at E_z was measured by the maximum bubble pressure method[16]. The charge density and surface tension in the presence of TMTU were obtained by the back integration of differential capacity–potential dependences[17].

RESULTS AND DISCUSSION

Analysis of Experimental Data

The parameters of the double-layer for TB adsorption in the presence of 0.05 M TMTU were based on the capacity data. The differential capacity–potential curves were obtained experimentally for ten concentrations of TB in base electrolytes consisting of 0.1, 0.5 and 1.0 M NaClO$_4$ with 0.05 M TMTU. Figure 1 presents the differential capacity–potential curves in 0.5 M NaClO$_4$ (*1*), 0.5 M NaClO$_4$ with 0.5 M TB (*2*) and 0.5 M NaClO$_4$ with 0.05 M TMTU for chosen concentrations of TB (solid lines), extrapolated to zero frequency. The analysis of these curves suggests a domination of TMTU adsorption. This is confirmed by the absence of TB adsorption peaks, which appear in the absence of TMTU. Additionally, an increase in TB concentration causes a slight decrease in differential capacity in the range from –0.6 to –1.2 V. The TB presence in 0.05 M TMTU solutions is accompanied by an increase in desorption peaks and their shift towards more negative potentials with increasing TB concentration. A lack of clear influence of NaClO$_4$ concentration on the course of differential capacity should be highlighted. The capacity–potential data were numerically integrated from the E_z point. The integration constants are presented in Tables IA and IIA. TB concentra-
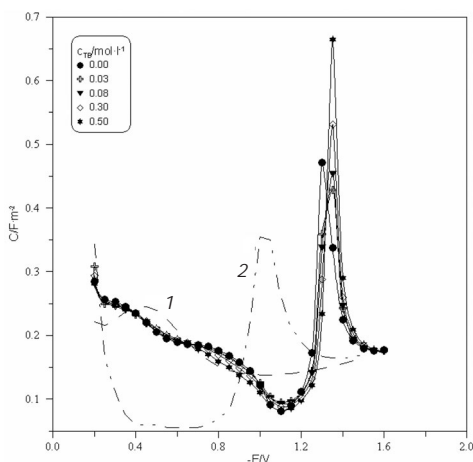

Fig. 1

Differential capacity–potential curves of the mercury electrode in contact with 0.5 M NaClO$_4$ (*1*), 0.5 M NaClO$_4$ with 0.5 M TB (*2*), and 0.5 M NaClO$_4$ with 0.05 M TMTU containing different concentrations of TB (solid lines)

tion increase causes a shift in the E_z value in the direction of less negative potentials, but these changes are relatively small compared with those in the absence of TMTU (Table IB). The $NaClO_4$ concentration has no influence on these changes when the TB concentration increases. In the absence of TMTU the total shift of E_z values with the increase of TB concentration change from –433.7 to –274.1 mV, from –457.3 to –272.8 mV and from –466.5 to –250.6 mV for 0.1, 0.5 and 1.0 M $NaClO_4$, respectively. The results confirm the adsorption of TB with -CH_3 groups placed on the mercury surface. A shift of E_z values in the direction of less negative potentials indicates that the TB dipole molecules adsorb at the electrode surface by the positive pole. Positive charge is placed on -CH_3 group in the TB molecule. On the other hand, a slight decrease in γ_z values with increasing TB concentration in the presence of TMTU is comparable with γ_z changes in the TMTU absence (Tables IIA and IIB). From the $q = f(E)$ dependences characteristic parameters of maximum adsorption; q_{max} as well as E_{max} are presented in

TABLE IA
The dependence of zero charge potential $-E_z$ vs Ag|AgCl electrode in the system $NaClO_4$ with 0.05 M TMTU and with TB

c_{TB}, mol l^{-1}	$-E_z$, mV		
	c_{NaClO_4}, mol l^{-1}		
	1.0	0.5	0.1
0.00	662.7	656.0	641.0
0.01	660.4	655.7	644.5
0.03	661.2	655.2	641.3
0.05	657.9	653.9	640.4
0.08	651.4	650.0	638.8
0.09	650.5	648.5	638.4
0.10	647.6	647.7	637.4
0.20	647.4	645.3	634.8
0.30	647.2	643.9	632.9
0.40	645.4	642.0	625.9
0.50	645.2	636.3	623.3

Table III. For comparison, the parameters in the absence of TMTU are also shown. These results indicate a reverse direction of changes of q_{max} and E_{max} with increasing $NaClO_4$ concentration. Therefore, the TMTU presence significantly changes the TB adsorption mechanism. The surface tension obtained by integration of differential capacity curves was subsequently used to calculate the surface pressure $\Phi = \Delta\gamma = \gamma_0 - \gamma$, where γ_0 is the surface tension for $NaClO_4$ with 0.05 M TMTU solution and γ is the surface tension for solutions containing also TB. Figure 2 shows plots of Φ versus $\ln c_{TB}$ for 0.5 M $NaClO_4$ with 0.05 M TMTU and selected electrode potentials, and the curve for $E = -0.5$ V in the absence of TMTU for comparison. The obtained values of Φ are smaller than in the absence of TMTU; they decrease in the order: $1.0 > 0.5 > 0.1$ M $NaClO_4$. It should be noted that the potential range of positive Φ values expands in comparison with TB adsorption from $NaClO_4$ solutions without TMTU. Moreover, the values of Φ increase monotonically in the direction of negative potentials. The values of Φ were

TABLE IB
The dependence of zero charge potential $-E_z$ vs Ag|AgCl electrode in the system $NaClO_4$ with TB

c_{TB}, mol l^{-1}	$-E_z$, mV		
	c_{NaClO_4}, mol l^{-1}		
	1.0	0.5	0.1
0.00	466.5	457.3	433.7
0.01	465.9	455.6	431.3
0.03	463.7	452.6	430.3
0.05	461.1	451.6	426.0
0.08	459.8	443.4	418.3
0.09	453.7	439.5	418.0
0.10	432.1	437.5	378.9
0.20	429.6	400.2	371.6
0.30	359.7	352.5	363.7
0.40	301.4	327.7	278.7
0.50	250.6	272.8	274.1

used to calculate the relative surface excess, Γ', which, according to the Gibbs adsorption isotherm, is given by

$$\Gamma' = \frac{1}{RT}\left(\frac{\partial \Phi}{\partial \ln c}\right)_E \tag{1}$$

where c is the bulk concentration of TB. In the derivation of Eq. (*1*), it was assumed that the activity coefficients of $NaClO_4$, TMTU and TB do not change with changes in TB concentration. The Γ' values obtained for 0.5 M $NaClO_4$ with 0.05 M TMTU, depending on the electrode potential and TB concentration, are presented in Fig. 3. The course of these dependences is totally different from the adequate dependences in the absence of TMTU. On the $\Gamma'_{TB} = f(E)$ curves in the absence of TMTU, a clear maximum at –0.5 V appears, whereas in the presence of 0.05 M TMTU, the Γ'_{TB} values increase in the direction of more negative potentials. This is undoubtedly

TABLE IIA

The dependence of surface tension γ_z at E_z in the system $NaClO_4$ with 0.05 M TMTU and with TB

c_{TB}, mol l^{-1}	γ_z, mN m^{-1}		
	c_{NaClO_4}, mol l^{-1}		
	1.0	0.5	0.1
0.00	385.2	378.5	389.0
0.01	384.5	386.9	388.7
0.03	383.2	386.4	388.5
0.05	382.5	385.9	388.0
0.08	381.5	385.6	387.6
0.09	380.2	385.0	387.1
0.10	379.3	384.7	386.6
0.20	378.4	384.3	386.5
0.30	377.6	383.8	385.1
0.40	376.5	383.5	385.5
0.50	375.1	382.3	385.0

the effect of a lower TMTU adsorption at more negative potentials. The Γ'_{TB} values are the largest in 1.0 M NaClO$_4$, whereas in 0.5 and 0.1 M NaClO$_4$ these values are comparable. These results confirm a stronger adsorption of investigated organic compounds in more concentrated base electrolytes also in the presence of mixed adsorption layers[10,11,18].

Adsorption Isotherms

The adsorption of TB in the presence of 0.05 M TMTU was further analyzed on the basis of constants obtained from the modified Flory–Huggins[19–22] isotherm for long-range particle–particle interactions

$$\beta x = \left[\frac{\Theta}{n(1 - \Theta)^{\,n}} \right] \exp(-2\,A\Theta) \tag{2}$$

TABLE IIB
The dependence of surface tension γ_z at E_z in the system NaClO$_4$ with TB

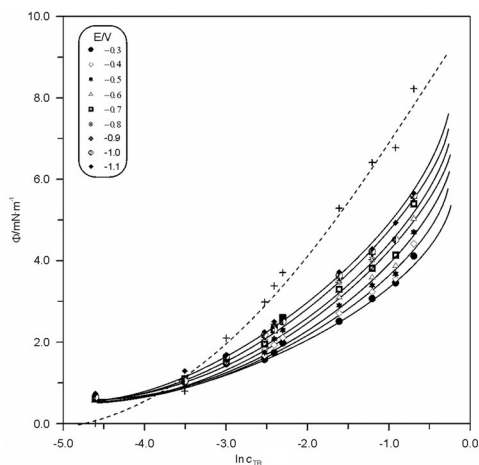| c_{TB}, mol l^{-1}	γ_z, mN m^{-1}		
	c_{NaClO_4}, mol l^{-1}		
	1.0	0.5	0.1
0.00	423.0	425.0	425.0
0.01	422.1	424.4	424.6
0.03	421.1	423.4	424.4
0.05	420.4	423.0	423.6
0.08	419.0	422.2	423.1
0.09	418.2	421.1	422.7
0.10	417.0	420.4	422.1
0.20	416.0	420.0	421.8
0.30	415.1	419.3	421.1
0.40	414.6	419.2	420.9
0.50	413.2	418.8	420.0

Fig. 2

Surface pressure Φ as a function of TB bulk concentration (in mol l^{-1}) for 0.5 M NaClO$_4$ with 0.05 M TMTU, and the curve for $E = -0.5$ V in 0.5 M NaClO$_4$ in the absence of TMTU (dashed line)
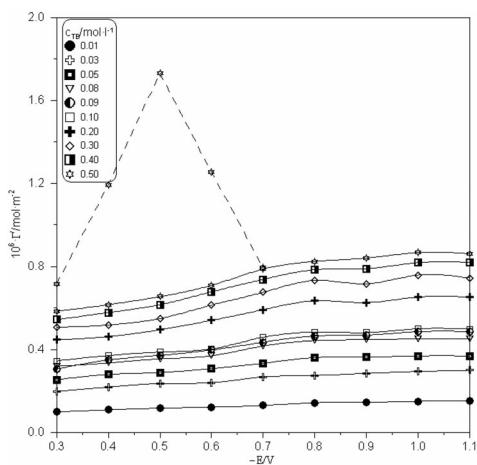

Fig. 3

Relative surface excess of TB as a function of the electrode potential and TB bulk concentration for 0.5 M NaClO$_4$ with 0.05 M TMTU (from bottom 0.01 to top 0.5 M TB), the Γ' values for 0.5 M TB in the absence of TMTU (dashed line)

where x is the molar fraction of TB in the solution ($x \approx c/55.5$), β is the adsorption coefficient ($\beta = \exp(-\Delta G^o/RT)$), ΔG^o is the standard energy of adsorption, A is the interaction parameter, Θ is the coverage, and n is the ratio of the surface occupied by the molecule adsorbed on the electrode and the surface of the molecule displaced from the electrode by one adsorbate molecule. The original Flory–Huggins isotherm describes the behavior of a two-dimensional lattice of non-interacting particles of different size[22]. However, if lateral interactions between different particles are different, then a particle at a given site tends to favor the occupation of the neighboring sites by those particles which interact more attractively. If the energy of solvent–solvent, solvent–solute and solute–solute interactions are assumed to be independent of coverage in constant electric state, then the adsorption behavior of a two-dimensional lattice of solvent and solute particles of different size is approximately expressed by the Flory–Huggins modified isotherm[20].

The surface excess at saturation Γ_s was estimated by extrapolating the $1/\Gamma'$ vs $1/c_{TB}$ dependence at different potentials, to $1/c_{TB} = 0$. The values of Γ_s are significantly greater than the theoretical value of 3.9×10^{-6} mol m^{-2}: 16.0×10^{-6}, 7.2×10^{-6} and 8.4×10^{-6} mol m^{-2} in 1.0 , 0.5 and 0.1 M NaClO$_4$, respectively. The Γ_s values were used to calculate the surface occupied by one TB molecule S ($S \equiv 1/\Gamma_s$). The surfaces were 0.10, 0.23 and 0.20 nm^2 in 1.0, 0.5 and 0.1 M NaClO$_4$. The obtained S values may be caused by a deformation of an adsorbed TB molecule in the electric field in the presence of TMTU. With the aim of defining the competitive adsorption mechanism in the examined systems, the values of total surface excess Γ were determined and compared with the adequate values of relative surface excess Γ'. The values of Γ' greater than those of Γ may suggest that by adsorbing TB it dis-

TABLE III
Maximum adsorption parameters q_{max} and E_{max} for TB

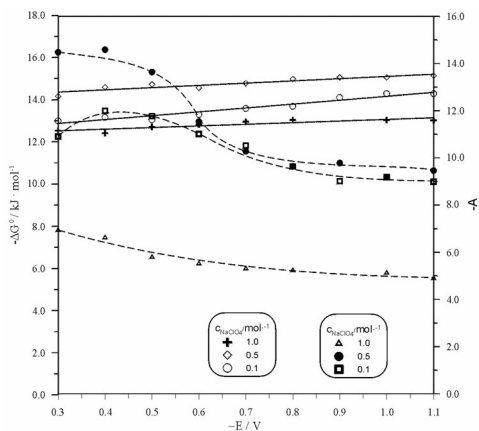| c_{NaClO_4} | 0 M TMTU | | 0.05 M TMTU | |
mol l^{-1}	$10^2 q_{max}$, C m^{-2}	$-E_{max}$, V	$10^2 q_{max}$, C m^{-2}	$-E_{max}$, V
0.1	−0.59	0.455	−5.16	0.974
0.5	−1.16	0.497	−5.06	0.949
1.0	−1.92	0.550	−1.02	0.700

F$_{IG}$. 5
Variation of the Gibbs energy of adsorption ΔG^o (solid lines) and of the interaction parameter
A (dashed lines) due to electrode potential and NaClO$_4$ concentration for TB in NaClO$_4$ with
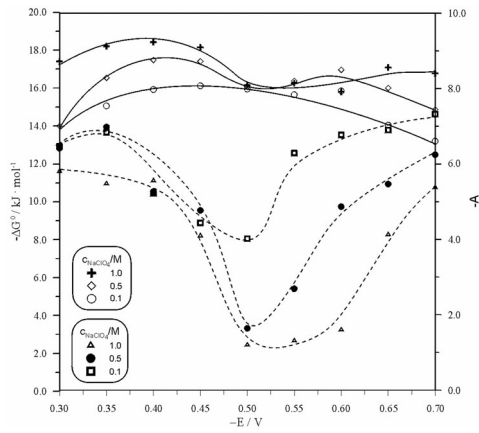0.05 M TMTU

FIG. 6
Variation of the Gibbs energy of adsorption ΔG^o (solid lines) and of the interaction parameter A (dashed lines) due to electrode potential and $NaClO_4$ concentration for TB in $NaClO_4$ in the absence of TMTU
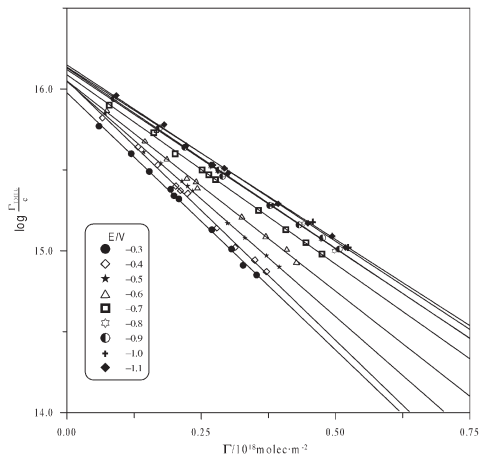

FIG. 7
Linear test of the virial isotherm for the system 0.5 M $NaClO_4$ with 0.05 M TMTU and with TB

places H_2O, but not TMTU, from the electrode surface. Therefore, the parameter n is the ratio of the surface occupied by TB molecules to that occupied by H_2O molecules. In the present case, using the projected area 0.123 nm^2 for water[21] and that for TB calculated from Γ_s, parameter n is 0.81, 1.87 and 1.63 in 1.0, 0.5 and 0.1 M $NaClO_4$, respectively. As ClO_4^- ions cause the strongest disruption in water structure[23], the surface of one water molecule is used in calculations instead of water clusters. Figure 4 shows the linear test of the modified Flory–Huggins isotherm for the chosen values of electrode potential in 0.5 M $NaClO_4$ with 0.05 M TMTU. The A values were calculated from the slopes of the lines shown in Fig. 4 and the corresponding values of ΔG^o were determined by extrapolation of the ln $\{[x(1 - \Theta)^n]/\Theta\}$ vs Θ dependence to $\Theta = 0$. The obtained results are presented in Fig. 5. The ΔG^o values slightly rise in the direction of more negative potentials. In the same direction, the repulsive interactions are even more weaker. Such changes of the adsorption parameters confirm the increase in relative surface excess towards negative potentials. On the other hand, the largest values of Γ' for TB in 1.0 M $NaClO_4$ are a result of the weakest repulsive interactions of adsorbed TB molecules. ΔG^o values in a small degree depend on $NaClO_4$ concentration and are the smallest in 1.0 M $NaClO_4$. Whereas in the absence of TMTU, the values of ΔG^o are highest
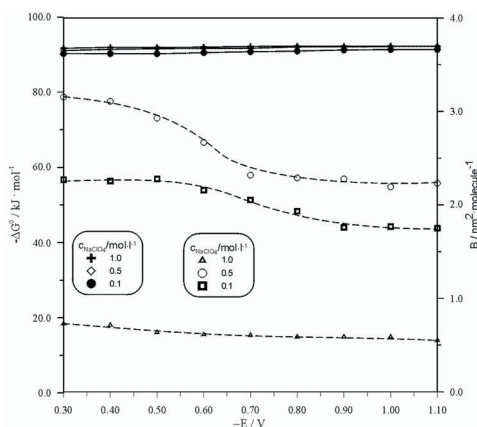

Fig. 8

Variation of the Gibbs energy of adsorption ΔG^o (solid lines) and of the interaction parameter B (dashed lines) due to electrode potential and $NaClO_4$ concentration for TB in $NaClO_4$ with 0.05 M TMTU, derived from virial isotherm

(Fig. 6). The changes of A parameter and ΔG^o in the function of electrode potential in the presence and in the absence of TMTU are clearly different. For TB at the Γ' maximal value, in the absence of TMTU (Fig. 3), the ΔG^o values do not depend on $NaClO_4$ concentration (Fig. 6). They are accompanied by the weakest repulsive interactions of adsorbed TB molecules.

The obtained data from the modified Flory–Huggins isotherm were verified using a virial isotherm. The application of virial isotherm does not need the knowledge of Γ_s. The virial isotherm equation is

$$\ln \beta c = \ln \Gamma + 2B\Gamma \tag{3}$$

where B is the two-dimensional (2D) second virial coefficient. Figure 7 shows the linear test of the virial isotherm for 0.5 M $NaClO_4$ with 0.05 M TMTU. The values of 2D second virial coefficient were calculated from the line slopes in Fig. 7, and the corresponding ΔG^o values were obtained from the intercepts of these lines on the axis log (Γ'/c) using the standard states 1 M in the bulk solution and 1 mol cm^{-2} on the surface. The obtained values of the virial constants are presented in Fig. 8. The ΔG^o values were practically independent from $NaClO_4$ concentration. The trend of changes of the B parameter is similar to the A parameter change in the Flory–Huggins isotherm.

CONCLUSIONS

1. The presence of TMTU has a positive influence on the possibility of extending the range of potentials in which TB adsorption parameters can be determined.

2. The physical character of TB adsorption in the presence of TMTU is weakened. An evidence is expressed by (i) the absence of maximum in $\Gamma'_{TB} = f(E)$ dependences and (ii) a characteristic slight increase in Γ'_{TB} values towards negative potentials which has not occurred in the studied systems so far.

3. Clearly higher Γ'_{TB} values obtained for 1.0 M $NaClO_4$ with 0.05 M TMTU compared with 0.5 and 0.1 M $NaClO_4$ containing TMTU. This effect complies with our previous results which confirm an increase in adsorption of investigated organic substances with increasing $NaClO_4$ concentration.

4. The weakest repulsive interaction of adsorbed TB molecules resulting from the smallest values of A and B parameters in 1 M $NaClO_4$ with 0.05 M TMTU, which could be the reason for the largest Γ'_{TB} values in this base electrolyte.

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