# POLAROGRAPHY OF IONS OF ALKALI METALS IN PROPYLENE CARBONATES

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Propylene carbonate (PC) has attracted the attention of research workers as a solvent with very valuable properties for a variety of practical applications [1, 2]. Electrochemical investigations on PC are so far not numerous [2, 3], and PC has practically escaped investigation as a solvent for use in polarography. The present work is devoted to an investigation by ourselves of the polarographic behavior of ions in the alkali metals in PC. The results obtained have been compared with corresponding data for aqueous solutions. The PC* was submitted to double distillation in vacuum, and for the experiments the middle fraction was chosen, which boiled within a range of 0.5°C. The moisture content in this, determined by the method given in [4], was less than 0.005%. The cations investigated were introduced into the solution in the form of perchlorates or chlorides (MeX). These anhydrous salts before use for measurement were placed for 24 h in a vacuum drying cabinet at 250°C. The base solution employed consisted of tetraethylammonium perchlorate, which was obtained from the corresponding bromide and sodium perchlorate. The preparation obtained was recrystallized 7-10 times [3] from doubly distilled water until a deposition potential in water of —2.7 V with respect to the saturated calomel electrode (sat.c.e.) had been attained. The polarograms were recorded using polarograph ON-102 using a free electrode arrangement, and a saturated calomel electrode as the comparison electrode, and a platinum electrode as the auxiliary electrode. The potential of a dropping electrode [4] was measured as the difference of potentials at the ends of the cell:

| I | II | III | IV |
|---|---|---|---|
| Dropping mercury electrode Hg | Propylene carbonate + 0.2 N $(C_2H_5)_4NClO_4$ + MeX | Water + 0.15 N $(C_2H_5)_4NClO_4$ | Saturated KCl, $Hg_2Cl_2$ Hg |

The investigated solution was thermostated in its cell at 25± 0.2°C, while the separation surfaces of II-IV were located outside the cell at room temperature (18-22°C). The rate of dropping of the mercury from the capillary and the dropping period amounted respectively to 1.04 mg/sec, and 6.3 sec for PC; and 0.96 mg/sec and 7.2 sec for water. Derived polarograms were obtained on the polarograph ON-101 using a 2-electrode scheme in relation to the potential of mercury in the investigated solution. During these investigations a capillary with scoop was employed, and the dropping period was 0.15 sec.

The cations of all the alkali metals in PC give well-developed waves. For lithium, sodium, and potassium perchlorates, and also for cesium chloride, which are sufficiently soluble, we have been able to show a linear dependence of the mean limiting current ($\bar{I}_l$) and a concentration (c) in the concentration range $5 \cdot 10^{-4}$-$5 \cdot 10^{-3}$ N.

*We wish to express our deep gratitude to A. L. Shapiro for making available to us the necessary quantity of PC.

TABLE 1. Some Results of an Investigation of the Polarographic Behavior of the Cations of Alkali Metals in PC and Water at 25°C

| Ion | $(\varphi_{1/2})_p$, V | $(d\varphi_{1/2}/dT)_p$, mg/deg | $\left(\frac{1}{\bar{I}_l}\frac{d\bar{I}_l}{dT}\right)_p$, %/deg | $D_p \cdot 10^5$, cm²/sec | $\frac{r_p}{r_w}$ | $\frac{RT}{F}\ln\frac{(\bar{I}_l)_w}{(\bar{I}_l)_p}$, V | $(\varphi_{1/2})_w$, V |
|---|---|---|---|---|---|---|---|
| $Li^+$ | —2,071 | 1,7 | 1,2 | 1,5 | 2,7 | 0,026 | —2,345 |
| $Na^+$ | —1.916 | 0,8 | 1,3 | 2,2 | 5,2 | 0,033 | —2,100 |
| $K^+$ | —2,020 | 0,5 | 1,4 | 3,3 | 4,1 | 0,031 | —2,123 |
| $Rb^+$ | —2,039 | 1,0 | 1,8 | — | — | — | —2,118 |
| $Cs^+$ | —2,031 | 0,2 | 1,3 | 6,7 | 2,0 | 0,021 | —2,092 |

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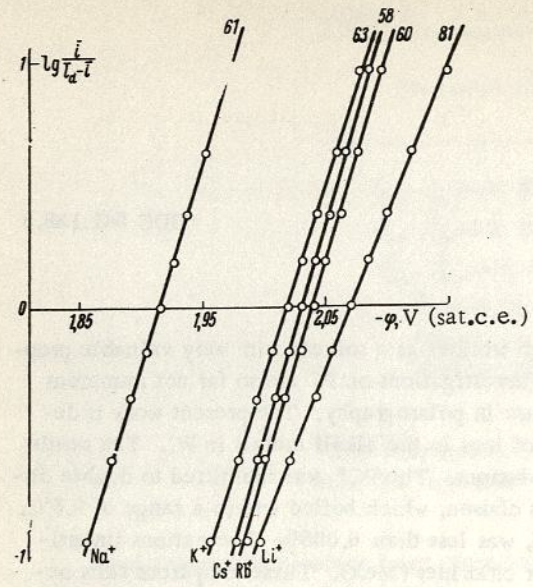


Fig. 1. Polarograms of $10^{-3}$ N solutions of lithium, sodium, and potassium perchlorates, and of cesium chloride and $\sim 5 \cdot 10^{-4}$ N rubidium chloride of the PC using a base of 0.2 N $(C_2H_5)_4NClO_4$. Temperature 25°C; $\varphi$ is measured in relation to an aqueous saturated calomel electrode.

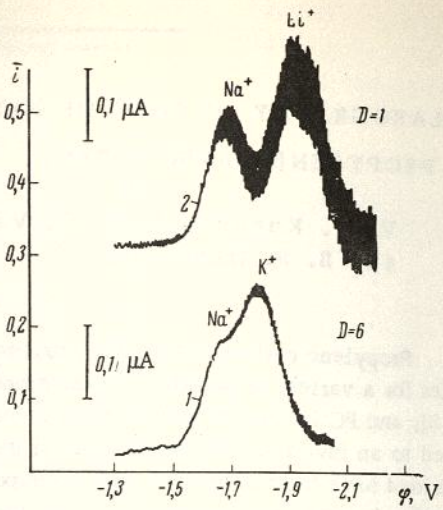


Fig. 2. Derived polarograms for sodium and potassium perchlorates [1] and for sodium and lithium ions [2] in PC, using as base 0.138 N $(C_2H_5)_4NClO_4$. Concentrations of sodium in both cases $1.33 \cdot 10^{-3}$ N, of lithium ion $2.0 \cdot 10^{-3}$ N, and potassium ion $2.0 \cdot 10^{-3}$ N. The damping of the apparatus in obtaining curve (1) was 6, and in the second case was 1; $\varphi$ is measured against mercury in the base of the cell.

The result obtained, and some values calculated from these, are shown in Table 1. The indices "p" and "w" refer to PC and water respectively; r is the radius of the solvated cation; D is the diffusion coefficient; $\varphi_{1/2}$ is the half-wave potential; and T is the absolute temperature. The values of the temperature coefficients of $\bar{I}_l$ found from the experimental work (Table 1) differ only slightly from the theoretical values of the temperature coefficients of the limiting diffusion current in PC (1.14%/deg), which we have calculated from the known values of the temperature coefficients of the viscosity of mercury of [5] and PC [6]. This indicates that $\bar{I}_l$ is of a diffusion character for the investigated cations, and taking into account the linear dependence $\bar{I}_l$ on c it is possible to calculate $D_p$ on the basis of the Il'kovich equation.

The values of $D_p$ (Table 1) for all the cations are appreciably lower than those of $D_w$, and this is not capable of being explained only by the larger viscosity of PC compared with water. It appears that in PC the value of r is greater than in water. If we assume that to a first approximation the following equation [7] is valid:

$$(\bar{I}_l)_p (r_p)^{1/2} (\eta_p)^{1/2} = (\bar{I}_l)_w (r_w)^{1/2} (\eta_w)^{1/2},$$

we have been able to calculate the ratio $r_p/r_w$ (Table 1). The term $\eta$ denotes the viscosity of the solvent.

Figure 1 shows in semilogarithmic coordinates the polarograms of the cations of the alkali metals at 25°C.

It can be seen from this figure that the polarographic curve can be well described by the Heyrovsky-Il'kovich equation. The values of the angular slopes (in mV) are shown by the corresponding straight lines in the upper part of the figure for the cases of the cations of sodium, potassium, rubidium, and cesium, and correspond to reversible single-electron reduction. In the case of the lithium ion the values of the coefficient is 81 mV, so that the wave of this cation in PC is partially irreversible. These conclusions have been confirmed by experiments using the Kalousec commutator.*

*The Kalousec commutator, which consists of a multivibrator using tubes 6N1P, was constructed and prepared by V. I. Veis, to whom we express our gratitude.

TABLE 2. Energy Effects for the Solvation of Cations (in kcal/mole) of Alkali Metals, and Difference in the Standard Potentials of These Metals in PC and in Water at 25°C

| Ion | $(\Delta\varphi_0)_w^p$ | $\Delta Z_w^p$ | $\Delta H_w^p$ [*] | $\Delta Z_w$ [*] | $\Delta H_w$ [*] | $\Delta Z_p$ | $\Delta H_p$ | $\Delta Z_w^p$ accord. to [11] |
|---|---|---|---|---|---|---|---|---|
| $Li^+$ | 0,248 | +2 1 | +3,2 | −24 | −26 | −22 | +23 | +5,1 |
| $Na^+$ | 0,153 | 0,0 | 0,0 | 0,0 | 0,0 | 0,0 | 0,0 | 0,0 |
| $K^+$ | 0,072 | −1,8 | −2,8 | +18 | +20 | +16 | +17 | +3,5 |
| $Pb^+$ | 0,058 | −2,3 | −3,4 | +23 | +26 | +21 | +23 | +0,5 |
| $Cs^+$ | 0,040 | −2,7 | −4,0 | +31 | +34 | +28 | +30 | −0,2 |

According to the equation in [7]:

$$(\varphi_0)_p - (\varphi_0)_w = (\Delta\varphi_0)_w^p = (\Delta\varphi_{1/2})_w^p - \frac{RT}{F}\ln\frac{(\bar{I}_l)_w}{(\bar{I}_l)_p},$$

which follows directly from the applicability of Heyrovsky-Il'kovich equation in the two solvents, we have calculated the difference between the standard potentials ($\varphi_0$) of the alkali metals in PC and in water, and from this also the difference in the free energies of solvation of the cations, $\Delta Z_w^p$, using as our standard that the corresponding values for the sodium ion is zero.

In [6], the differences in the enthalpies of solvation, $\Delta H_w^p$, were obtained. By using these values and the table of the most probable values of the chemical heats and energies of hydration of the individual ions [8], we have calculated the enthalpy and free energies ($\Delta H_p$ and $\Delta Z_p$, respectively) of solvation of the cations of the alkali metals in PC, once again taking the corresponding values for sodium ion as equal to zero.

It can be seen from Table 2 (where the values of $(\Delta\varphi_0)_w^p$ are positive) that the change in the free energy on the solvation of the investigated cations in PC is less than in water. This difference diminishes in moving from lithium to cesium. As also for all solvents investigated in [8], the difference between $\Delta H$ and $\Delta Z$ for solvation in PC is not considerable.

The negative potentials in which we observe the reduction of the ions of the alkali metals in PC is narrower than in the case of water, amounting to approximately 100 mV. However, the difference in $\varphi_{1/2}$ for sodium and for potassium ions is greater than the corresponding value in water. Figure 2 (curve 1) shows that on the derived polarogram, the maxima for potassium and sodium ions in PC are separated, and with sufficiently good technical differentiation, PC may be used for the separate determination of sodium and potassium ions when these are present simultaneously. The same may be said of sodium and lithium ions (Fig. 2, curve 2), since clear waves for lithium ions are obtainable considerably more easily in PC than in water.

At the time that the present article had been prepared for the press, a further article [9] appeared, in which it was made known that the authors of this article had already investigated the polarographic behavior of the ions of the alkali metals in PC, and had published a table of $\varphi_{1/2}$ values in [10]. Comparison of the data of the recently published additional communications [11] with our own data showed that in both cases the same conclusions were drawn about the nature of the electrode processes and the limiting currents, while the data obtained from measurements of $\bar{I}_l$ did not contradict each other. On the other hand, the values of $\varphi_{1/2}$ determined in our present work are clearly in disagreement with those in [11]. In particular, according to our own data, sodium ions are reduced more easily than potassium ions, while the opposite result is obtained from the data in [11].

In Fig. 2 we give what seems to us sufficiently convincing evidence that the order of reduction of the ions is actually that which is found in a present work. It should also be observed that the results of calculating the values of $\Delta Z_w^p$ which we have carried out from the data in [11] (last column in Table 2) are in worse agreement with the results obtained in [6] than our own data. The possible reason for the divergence found may be errors associated with the use of a two-electrode scheme in [11], which only serves to emphasize the problem involved in the introduction of "Corrections" for the values of the potentials found in the cell.

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