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A new simple sensitive differential pulse polarographic method for the determination of acrylamide in aqueous solution

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Received 13 August 2007; received in revised form 5 October 2007; accepted 5 October 2007

Available online 13 October 2007

Abstract

A new simple sensitive differential pulse polarographic (DPP) method was investigated for the determination of acrylamide (AA) directly in a neutral aqueous solution. The AA showed a well-defined and well-resolved peak in pure aqueous LiCl at -1.84 V in the potential range from -1.6 V to -1.97 V at nitrogen pressure of 0.5 kg cm^{-2} . Among the various electrolytes studied, the AA showed good DPP response in the presence of LiCl and tetra methyl ammonium iodide, while it showed poor response in the presence of tetra butyl ammonium hydroxide and tetra butyl ammonium bromide due to their strong adsorption on the surface of electrode which hindered its reduction. The effect of LiCl concentration, the cyclic voltammetric response and the drop time study showed that AA exhibited an irreversible adsorptive electrochemical behavior. The good electrochemical response in pure aqueous medium suggested that hydrogen bonding might be involved which may favor the electrode reaction. Under optimized conditions, the peak current was linear in the entire concentration range from 0.2 mg L^{-1} to 20 mg L^{-1} with the correlation coefficient of $R^2 = 0.9998$. The method showed good reproducible results with R.S.D. of 0.3% ($n = 16$). The detection limit (LOD) was $27 \text{ } \mu\text{g L}^{-1}$. The influence of various interfering agents was also studied. The method was applied successfully for the quantification of AA in water samples without any interference effect from alkali metals.

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Keywords: Acrylamide; Differential pulse polarography; Aqueous solution; LiCl; Water samples

1. Introduction

Acrylamide is an important industrial organic compound which is used in a wide number of processes [1]. It is used in the production of polymers (polyacrylamide) and copolymers for various purposes. Polyacrylamide is mainly used for the purification of both drinking and waste water, where it acts as a flocculating agent. In paper industries it is used to enhance resistance to tearing. It has numerous applications in petroleum and textile industries. AA is also used as a grouting agent in concrete and in mineral processing [2,3].

It is used in the construction of dam foundations and tunnels. Besides its importance, it is also very much toxic and constitutes serious water pollution problems. Due to high solubility in water, AA is extremely mobile in aqueous environment. The main sources of water contamination result from the release of monomer residues from polyacrylamide used in water treatment, soil grouting and polymer industries, etc. It has been studied that heat, light and out-door environmental conditions promote depolymerization of polyacrylamide to AA [4]. The toxicity of AA have been stated already by the International Agency for Research on Cancer (IARC) that AA could be classified as “probably carcinogenic to humans” (group 2A) [5] and the World Health Organization (WHO) guideline value associated with a lifetime cancer risk in drinking water [6].

The US Environment Protection Agency (EPA) set the maximum contaminant level (MCL) for AA at zero and requires the water supplier to show that when AA is added to water, the

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amount of un-coagulated acrylamide is less than $0.5 \mu\text{g L}^{-1}$ [7]. Due to its high toxic effects to humans and animals it is very much necessary to establish a simple, rapid, sensitive, highly selective analytical methodology for the direct quantification of AA in aqueous solution.

A variety of sensitive methods are available in the literature to analyze AA in aqueous solutions [8–14]. Most of these methods are based on the techniques such as HPLC–UV, GC–MS and LC–MS/MS. Derivatization of AA prior to analysis and large efforts involved in sample preparation come as disadvantages with the use of these techniques. The others major disadvantages of these methods are their high equipment costs and running costs. Recently, direct electrochemical detection following liquid chromatography has been proposed for the determination of AA in aqueous samples [15].

But in terms of simplicity, selectivity, relatively good sensitivity, without any derivatization, it carries very low running and equipments costs and is easily available in under developed areas, however, the electro analytical techniques, mainly DP polarography, are the most suitable techniques for the determination of AA in complicated matrices as compared to the other nonelectroanalytical techniques [16].

But unfortunately there is no sensitive polarographic method available which could monitor AA directly at a trace level in aqueous solution [1], and till now. All the previously polarographic methods for the determination of AA in different matrices have been reported in nonaqueous or mix solvent system [17–25]. Among these methods the most efficient polarographic method till now has been reported by Betso and McLean to determine AA monomer in polyacrylamide containing 80/20 methanol/water [17]. They modified the polarographic method of McWilliams et al. [20] by using more advance instrumentation (differential pulse polarograph instead of the older direct-current instrument). By using this instrumentation the AA reduction peak became well-defined and well-resolved from the background. They lowered greatly the detection limit to less than 1 mg L^{-1} (0.5) in relation to all previously reported polarographic methods for the determination of AA.

However, this method suffer from serious drawbacks for example this is not suitable to monitor AA directly in aqueous solution, less sensitive and at -2.0 V it suffer from major interferences mainly from the alkali metals cations. Therefore, a more sensitive and selective polarographic method is essential to determine AA directly in aqueous solution. To our best knowledge this is the first time that we have investigated a simple sensitive, selective polarographic method for the quantification of AA directly in aqueous solution.

2. Experimental

2.1. Reagents and solution

All reagents were of analytical grade. Acrylamide (electrophoresis grade) and LiCl were purchased from Merck Germany. Other reagents used in this study were also purchased

from the same company. All solutions were prepared in double distilled water. A stock solution of 1000 mg L^{-1} AA was prepared from which appropriate amount was taken for polarographic studies. Five molar LiCl solution was also prepared in a separate flask which was used as an electrolyte and carrier solution.

2.2. Apparatus

Polarographic experiments were performed by Metrohm polarographic analyzer (Switzerland) model 797 version 1.1 with a personal computer. A typical three electrode system equipped with a dropping mercury working electrode, a platinum counter electrode and Ag/AgCl/3 M KCl as a reference electrode. Nitrogen was used as an inert gas to purge the analyte solutions and to operate the mercury electrode. The optimum nitrogen gas pressure of 0.5 kg cm^{-2} (0.49 bar) was used through out in this study. In the instrumental setup the voltage step time (drop time) automatically controlled the sweep rate. When the voltage time was made to increase the sweep rate decreased accordingly.

2.3. Procedures

2.3.1. Polarographic studies

A volume of 10 mL flask solution containing 5 mg L^{-1} AA ($50 \mu\text{g L}^{-1}$ of 1000 mg L^{-1} stock solution) in 0.5 M LiCl electrolyte (1 mL of 5 M LiCl) was transferred into a polarographic cell. After purging the solution with nitrogen for 5 min the polarograms were taken by scanning the potential from -1.6 V to -1.97 V at a voltage step time of 1.8 s, drop size 5, pulse amplitude of 0.05 V, pulse time of 0.04 s, voltage step of 0.006 V, sweep rate of 0.0033 V/s , peak potential of -1.84 V and nitrogen pressure of 0.5 kg cm^{-2} (0.49 bar). The reversibility of the electrode reaction was tested by using cyclic voltammetry on the same instrument at a scan rate of 0.055 V/s . All the AA analyses and the linear calibration curves were carried out by using standard addition method. All the measurements were performed at room temperature ($25 \pm 5^\circ\text{C}$).

2.3.2. Determination of acrylamide in water sample

For method validation a recovery tests were accomplished in local tape water for the quantification of AA in low, middle and high concentrations ranges using differential pulse polarography. A volume of 10 mL local tape water containing known amounts of AA in 0.5 M LiCl (1 mL of 5 M) were placed in a polarographic cell. Then for DPP measurements, the same conditions as mentioned previously, were performed and the amounts were calculated by using standard addition method. The concentrations of AA were also tested in the polymeric industrial discharge samples obtained from rubber and others petrochemical industries of Karachi, Pakistan.

The determinations of AA in these polymeric discharges were performed by employing the same polarographic procedure as described already. To test the matrix effect in these samples,

three successive additions of $0.001 \mu\text{L}$ of 1000 mg L^{-1} AA were spiked containing a known amount of 0.2 mg L^{-1} AA.

3. Results and discussion

To investigate the reduction of AA in various suitable supporting electrolytes, a broad differential pulse polarographic study was carried out in the potential range from -1.4 V to -2.4 V in aqueous solution. The peaks of AA were observed in the presence of some useful supporting electrolytes, but these peaks were found to be depressed completely due to high reduction current of the supporting electrolyte cations at about -2.0 V when broad potential range was employed.

Therefore, the study was performed by employing short potential range, i.e. from -1.4 V to -1.97 V instead of -1.4 V to -2.4 V broad potential range, in order to avoid the effect of high reduction current resulting from the supporting electrolyte cations at -2.0 V . By employing this short potential range, some well-defined and well-resolved peaks appeared to be observed and not depressed before the reduction of electrolyte cations, illustrated in Fig. 1. Thus in this study the selection of proper potential range from -1.4 V to -1.97 V was critical to investigate the peak current of AA in pure aqueous solution.

From Fig. 1 it can be seen that in the presence of tetra butyl ammonium bromide (TBAB) as a supporting electrolyte two polarographic peaks (A1 and A2) were obtained. The poorly defined peak (A1) at -1.90 V may be due to the reduction of AA and another relatively well-defined peak (A2) at -1.62 V may be due to the adsorption of electrolyte on the surface of electrode.

The adsorption peak (A2) attributed to TBAB at -1.62 V was further confirmed in the absence of AA. The broad and much poorly defined peak was obtained at -1.88 V in the case of TBAOH electrolyte, shown by curve (B). A relatively well-defined and well-resolved peak from the background at -1.86 V was obtained when tetra ethyl ammonium iodide (TEAI) was

used which is shown by curve (C). The peak obtained at -1.87 V in lithium chloride was also well-defined and became increased, shown by curve (D). The maximum peak height at a peak potential of -1.86 V was obtained in TMAI, represented by curve (E).

These results indicate that the type of supporting electrolyte cation has a considerable influence on the reduction of AA by changing the double layer structure of the electrode solution interface. By the addition of quaternary ammonium (R_4N^+) salts/hydroxide into the solution, the peak current became increased and the peak potential shifted toward more negative values as when the size of R-group (R_4N^+) was increased. This effect may probably attribute to the specific adsorption of R_4N^+ at the surface of electrode. The adsorbability of tetra alkyl ammonium ions (R_4N^+) increases in the order $\text{TMA} < \text{TEA} < \text{TBA}$ [26,27]. The results reveal the obvious fact that the reduction of AA consumes protons from the surface of electrode and it was hindered by the adsorption of tetra butyl ammonium cations from TBAB and TBAOH electrolytes.

The size of the electrolyte cations has also shown a considerable influence on the rate of reduction of AA. The high reduction current at less negative potential was observed in the case of TMAI and then in LiCl as shown in Fig. 1. The effect of LiCl concentration on the reduction of AA was observed to be more pronounced as compared to TMAI because of its less adsorbability on the surface of electrode and its high solubility in aqueous medium.

The effect of LiCl concentration on the peak current and peak potential of AA was studied as shown in Fig. 2. The peak current increased gradually with the increasing concentration of LiCl from 0.005 mol L^{-1} to 0.5 mol L^{-1} , but at the same time the peak potential shifted towards less negative values. Then both the peak current and peak potential remained constant, while the peak width became broader after when the concentration of LiCl was increased from 0.5 mol L^{-1} to 1.75 mol L^{-1} . This showed that the reduction peak current of AA was strongly dependent on LiCl concentration thereby changing the double layer structure of the electrode solution interface. The effect of TMAI concentration on peak current of AA was also studied and the maximum peak current was obtained in 0.2 M without any shift of peak potential.

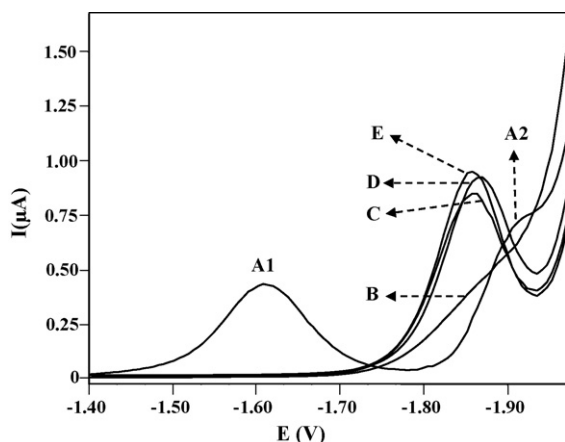


Fig. 1. Polarographic behavior of acrylamide in some useful supporting electrolytes in pure aqueous solution. (A) (A1 and A2) TBAB, (B) TBAOH, (C) tetra ethyl ammonium iodide (TBEI), (D) LiCl and (E) TMAI. The concentrations of all the supporting electrolytes used were 0.05 M . Potential range from -1.4 V to -1.97 V , drop size of 5, voltage step time of 1 s.

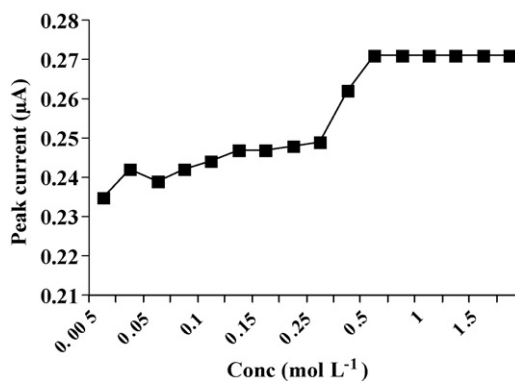


Fig. 2. Effect of LiCl concentration on the peak current of 5 mg L^{-1} acrylamide. Initial potential: -1.4 V ; end potential: -1.97 V ; voltage step time: 0.4 s ; drop size: 4.

But the peak current obtained in TMAI was found to be low than the peak current obtained in LiCl.

This result also confirmed that replacing a cation in the supporting electrolyte by another more strongly absorbable one, e.g., (lithium by tetra methyl, tetra methyl by tetra ethyl and tetra ethyl by tetra butyl) caused the shifting of peak potential towards more negative value, whereas the peak current decreased or even absent, in the reduction of cationic AA. This result is consistent with the previous results [27,28], but in this case the electroactive species is cationic (AA) rather than anionic which displaced the peak potential towards more negative values due to electrostatic repulsion between cationic AA and tetra butyl ammonium cation adsorbed at the surface of electrode. The AA showed the highest sensitivity at less negative potential in the presence of LiCl because of its lowest adsorbability at the surface of electrode due to small size. So LiCl of 0.5 M was chosen as a useful supporting electrolyte for the reduction of AA.

3.1. Cyclic voltammetric study

In order to check the reversibility of the electrode reaction, cyclic voltammogram (CV) of 10 mg L^{-1} AA in 0.5 M aqueous LiCl at a scan rate of 0.055 V/s was recorded. It can be seen from Fig. 3, that cathodic peak of AA appeared at about -1.85 V and there was no anodic peak appeared in the reverse scan, indicating the totally irreversible nature of the electrode reaction.

3.2. Effect of voltage step time (drop time) on the reduction current of AA

To elucidate the kind of electrode reaction the effect of voltage step time was studied. The peak current of AA increased gradually and the peak potential shifted towards less negative values with an increase in the voltage step time from 0.4 s to 2.6 s , while beyond this range it abruptly decreased in the form of distorted peak due to increased current oscillations.

The distortion of peak shape due to increased amplitude of current oscillations started after when the voltage step time was increased from 2.2 s to 3 s . The increase in peak current with an increase in voltage step time indicated that the limiting current was partly controlled by the rate of potential scan or drop time. This suggests an adsorptive chemical reaction involving a relatively slow step on the surface of electrode. Such type of reaction

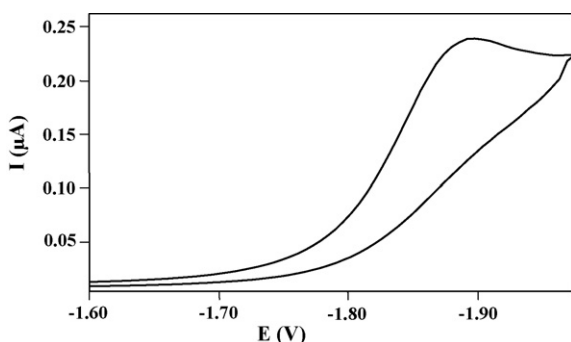


Fig. 3. Cyclic voltammogram of AA in pure aqueous solution of 0.5 M LiCl. Scan rate: 0.055 V/s .

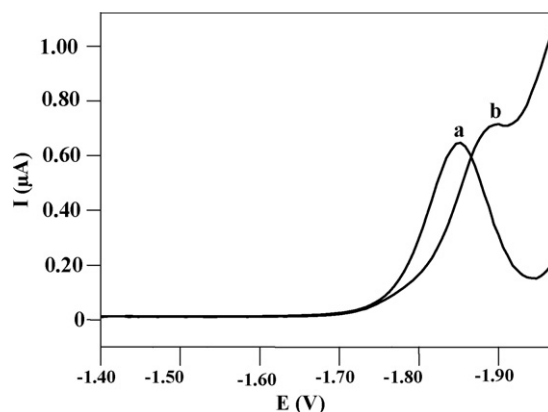


Fig. 4. Comparison of the reduction of AA (a) in pure aqueous solution and (b) in 80:20 methanol/water containing the same solution of 0.5 M LiCl in the potential range from -1.40 V to -1.97 V .

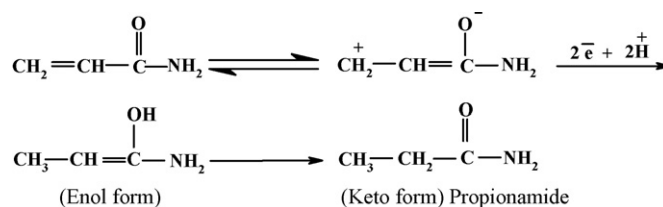
involving a slow step need not be observable further with dropping mercury electrode (DME) because there is a time limit for measurement and the rate of potential scan cannot be widely varied. The current oscillations may also result due to complete coverage of the reaction product at the electrode surface which inhibits the electrode reaction when using long voltage step time.

However, a voltage step time of 1.8 s at a sweep rate of 0.0033 m/s was selected for further study, because it completely avoided the deformation of peak attributed to the long voltage step time and also minimizing the time scale of measurement.

Fig. 4 shows the comparison between the peak current obtained in pure aqueous solution and the peak current obtained in 80% methanolic mixture containing the same solution of 0.5 M LiCl supporting electrolyte. A well-defined and well-resolved DPP peak was obtained at -1.84 V in pure aqueous solution (a), while a poorly defined DPP peak was obtained at -1.87 V in 80% methanolic mixture (b). This indicated that pure aqueous medium facilitates the reduction of AA in comparison to methanolic mixture.

The mechanism of the electrode reaction for AA as has been described already in neutral methanolic solutions of TMAI or LiCl [18]. It has been found that double bond becomes saturated by the addition of two protons and two electrons. Later on, it was suggested that neither the double bond nor the amide group would be reducible, and that the electronic conjugation of these two brings about a mesomeric electron shift towards the carbonyl oxygen, producing a keto–enol rearrangement allowing the reduction to propionamide.

In the reaction (Scheme 1) the equilibrium favors the keto form since the sum of its bond energies is higher than that of enol form. It has also been described that enolization is affected



Scheme 1.

greatly by water which reduces the enol form by hydrogen bonding with the carbonyl thereby reducing the propensity for internal hydrogen bonding [29]. So from all these results it was concluded that in pure aqueous solution the electron proton transfer kinetics of AA takes place more easily by stabilizing greatly the electrode reaction product via hydrogen bonding.

Moreover, the nitrogen pressure also affected the peak current of AA. It was observed that by increasing the nitrogen pressure above from 0.5 kg cm^{-2} (0.49 bar) the noise level or current oscillations in the peak current became more pronounced as a result of distorted peak was found rather than well-resolved peak. Thus the nitrogen pressure was also found to be a significant factor to investigate the peak current of AA in aqueous solution.

Therefore the nitrogen pressure of 0.5 kg cm^{-2} was selected for further study because this showed best results in terms of peak shape and peak current. Moreover the drop size of 5 was optimized for further experiments because it showed relatively good sensitivity for AA.

After all the experiments, the conditions optimized for the determination of AA in aqueous solution were the use of dropping mercury electrode (DME) as a working electrode with DPP mode, initial purge time of 300 s, drop size of 5, start potential of -1.6 V , end potential of -1.97 V , peak potential of -1.84 V , pulse amplitude of 0.05 V , pulse time of 0.04 s , voltage step of 0.006 V , voltage step time of 1.8 s , sweep rate of 0.0033 V/s and nitrogen pressure of 0.5 kg cm^{-2} .

3.3. Analytical performance of the method

3.3.1. Linear calibration curve

Calibration plot for AA was carried out under the optimized conditions using DPP in aqueous solution of 0.5 M LiCl . The reduction peak current for AA was linearly proportional to the AA concentration in the range from 0.2 mg L^{-1} to 20 mg L^{-1}

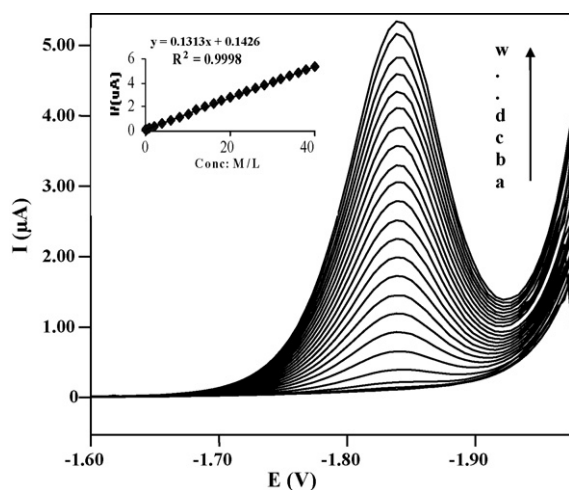


Fig. 5. DPP of AA in aqueous solution of 0.5 M LiCl containing: (a) 0, (b) 0.2, (c) 0.8, (d) 2, (e) 4, (f) 6, (g) 8, (h) 10, (i) 12, (j) 14, (k) 16, (l) 18, (m) 20, (n) 22, (o) 24, (p) 26, (q) 28, (r) 30, (s) 32, (t) 34, (u) 36, (v) 38 and (w) 40 mg L^{-1} AA. In the calibration curves after 0.8 mg L^{-1} (curve c), the same successive additions of 2 mg L^{-1} AA were carried out from curve (d) to curve (w).

with the correlation coefficient of $R^2 = 0.9998$. The calibration curve shown in Fig. 5, demonstrated good linear relationships between the concentrations and peak currents over the entire concentrations range. This indicated that the promoting reduction process did not block the surface of electrode even in this high concentrations range. This suggested that the method could be applied in the broad range of concentrations.

This result also indicated that the method could be sensitive for the quantification of AA in aqueous solution. The limit of detection (LOD) was calculated by using the equation:

$$\text{LOD} = 3(s/S) \quad (1)$$

where “s” is the standard deviation of the response (blank) and “S” is the slope or sensitivity of the calibration curve at levels approaching the limit. The standard deviation “s” of the same solution of seven blank measurements was found to be $0.0012 \mu\text{A}$ and the slope value “S” of $0.1313 \mu\text{A}$ obtained from the calibration curve. By putting these values in Eq. (1), the detection limit of $27 \mu\text{g L}^{-1}$ was obtained and this is the concentration of AA that gave a signal three times the standard deviation of the background signal [30].

The reproducibility of the proposed method was evaluated by repeating 16 successive DPP measurements of the same solution of 5 mg L^{-1} AA in 0.5 M LiCl . The mean peak current value ($n = 16$) at a peak potential of -1.84 V was found to be $780 \pm 2.4 \text{ nA}$ with R.S.D. of 0.3% . This demonstrated the reproducibility and stability of the method.

3.3.2. Interference study

The influence of various likely interferences was tested by analyzing a standard solution of 5 mg L^{-1} AA in the presence of 0.5 M LiCl . These interferences were some carbonyl or unsaturated organic compounds and alkali metals cations. The interference effects of these agents in the presence of 5 mg L^{-1} AA in aqueous solution of 0.5 M LiCl are illustrated in Table 1.

The solutions containing different interferences to AA ratios in the range of 1:1–200:1, as given in Table 1, demonstrated that all the values obtained were within $\pm 5\%$.

In this study the reduction of AA occurred at a peak potential of ca. -1.84 V before the reduction potentials of Ca^{++} (-2.22 V), K^+ (-2.10 V) and Na^+ (-2.07 V) by about 380 mV , 260 mV and 230 mV , respectively.

This showed that the difference between the peak potential of AA and the reduction potentials of alkali metals were suffi-

Table 1
Effect of interfering species on AA determination by using DPP

| Interferent | Interferent to acrylamide ratio | Deviation (%) DPP |
|------------------|---------------------------------|-------------------|
| Formaldehyde | 200:1 | +4.2 |
| Acetone | 50:1 | +4.8 |
| Acrolein | 1:1 | −3.7 |
| Acrylic acid | 2:1 | −4.1 |
| Maleic acid | 1:1 | −2.6 |
| Na^+ | 20:1 | +5 |
| K^+ | 25:1 | +3.8 |
| Ca^{++} | 50:1 | +2.7 |
| NH_4^+ | 50:1 | +4.9 |

Table 2
Determination results for acrylamide in local tape water

| Sample no. | Acrylamide added ($\mu\text{g mL}^{-1}$) | Acrylamide found ^a ($\mu\text{g mL}^{-1}$) | Recovery (%) |
|------------|--|---|--------------|
| 1 | 0.5 | 0.49 | 98.1 |
| 2 | 5.0 | 4.97 | 99.4 |
| 3 | 10.0 | 10.2 | 102 |

^a Average of five determinations.

ciently high which could allow the determination of AA in the presence of alkali metals cations. However, it was observed that at low concentration of AA in the presence of relatively high concentration of Na^+ and K^+ , the peak became depressed without any change in peak current. This was due to the high final current rise of the background current resulting from these metals which started before the final background current of LiCl electrolyte.

The owns of the final background or residual current resulting in the presence of alkali metals cations depends on their reduction potentials which decreases in the order $-2.31\text{ V} > -2.22\text{ V} > -2.10\text{ V} > -2.07\text{ V}$ for Li^+ , Ca^{++} , K^+ and Na^+ , respectively. As the reduction potentials of Na^+ and K^+ are lower than others, so their final background currents started earlier than Li^+ . Thus this was due to this reason that the peak became affected in the presence of these metals.

The effect was seen more in the determination of sufficiently low concentration of AA. In such a situation an accurate results were obtained by recording first the blank solution without analyte and then the solution containing analyte or using extrapolation method [31]. However, by the proposed method we could determine AA at a very low concentration in the presence of relatively high amount of Na^+ and K^+ .

3.3.3. Sample analysis

In order to assess the possible applications of the proposed method for the determination of AA, the samples consisting of known amount of AA in local tape water was tested. When known amounts of AA added to the water control samples using standard addition method, quantitative recoveries of 98.1–102% were obtained as listed in Table 2. The values shown in Table 2 presented a relative error lower or equal to 2%. Thus the accuracy of the investigated method in pure aqueous solution was evident.

AA was also analyzed in polymeric industrial discharges samples collected from polymeric industries of Karach. But we could not find AA, as the concentration of AA in these discharged samples may be absent or low than the detection limit of the proposed method. In order to test the matrix affects in these polymeric discharges, a known amount of $0.2\text{ }\mu\text{g mL}^{-1}$ AA was spiked using standard addition method. From this a quantitative recovery of 96% was obtained which showed a good selectivity of the proposed method.

4. Conclusion

After a long time, a new simple differential pulse polarographic method was investigated. The new proposed method offered rapidity, sensitivity and highly selectivity for the deter-

mination of AA directly in aqueous solution of LiCl. In this study the selection of proper potential range and applied nitrogen pressure to mercury electrode were important factors to investigate a well-resolved peak of AA in aqueous solution. The AA showed good response in the presence of LiCl or TBAI while it showed poor response in the presence of TBAOH and TBAB due to hindrance effects. The electrode reaction was found to be more favorable in pure aqueous solution which might be attributed to the hydrogen bonding thereby stabilizing greatly the reaction product. The sensitivity was greatly improved than the previously reported methods. Although the detection limit $27\text{ }\mu\text{g L}^{-1}$ is not sufficient to verify the compliances with WHO guidelines and EPA recommended estimation of $0.5\text{ }\mu\text{g L}^{-1}$ in drinking water and also not competable with the advance instrumental techniques. But however, the proposed method could open a new field of research for more sensitive investigations of AA in pure aqueous medium at this very simple, inexpensive technique which would be compatible to the advanced techniques.

Acknowledgements

We express our gratitude to Professor Michael Heyrovsky, Heyrovsky Institute of Physical Chemistry, Prague, Czech Republic for his valuable suggestions, and Professor Maher Kalaji, School of Chemistry, University of Wales, Bangor, Gwynedd, UK for updating our electrochemical approaches.

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