S K Rangarajan

Biographical Sketch and Scientific Contributions

M V Sangaranarayanan

This article provides a brief biographical sketch as well as highlights a few selected scientific contributions of Prof S K Rangarajan who passed away in Bangalore recently. The diverse nature of the research contributions ranging from functional analysis and stochastic modeling to corrosion phenomena and impedance spectroscopy is emphasized.

Sarukkai Krishnamachari Rangarajan ('SKR') had many facets to his scientific pursuits and outlook. It is not often that one comes across an individual whose research investigations range from functional analysis and stochastic modelling to ion transport across membranes and bipolar cells – the accomplishments themselves resulting from no 'formal' training/background of any type. For those who had the privilege of knowing him at close quarters, he was truly a genius. He had deep insights underlying any research problem and hence was able to provide entirely novel analyses pertaining to them. A few of the research topics which engaged his attention for an extended period of time were: Special functions and mathematical analysis, Faradaic rectification; non-linear relaxation techniques, systems analysis, electrocrystallization, electrical double layer; quantum electrochemistry and many-body theory, photoelectrochemistry, porous electrodes, current distribution and roughness; inverse problems, superoperator formalism and Green functions, Pade' approximants. The path-breaking results arising out of his rigorous and intuitive analysis were of direct relevance to several areas in applied electrochemistry such as corrosion of metals, and current distribution in bipolar cells. His work on accelerated Tafel plots provided an entirely new perspective to the field of electrode kinetics. During the past few years, he was deeply engrossed in the de-mystification of several identities proposed

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Electrochemical systems, mathematical analysis.

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by Ramanujan on divergent series as well as new methods of computing Riemann zeta functions.

Education and Initial Assignments

After graduating with a BA (Hons) in mathematics in 1953 from Madras Christian College (MCC), SKR was appointed as a tutor in MCC; subsequently he joined as an Assistant Professor at the Alagappa Chettiar college of Engineering and Technology in Karaikudi. During this brief period, he was constantly improvising advanced mathematical techniques and applied them to a variety of physico-chemical situations. He could derive novel identities pertaining to polynomials of Legendre, Laguerre, Angelescu, Tricomi *genre'*. During his tenure at the Central Electro Chemical Research Institute (CECRI) Karaikudi, where he joined at the persuasion of Prof K S G Doss (then Director of CECRI), his focus shifted to the modeling of electrochemical systems in conjunction with the development of new experimental techniques for kinetic and mechanistic studies. SKR served for about ten years (1960–1970) at CECRI in the fundamental electrochemistry division. He was a Founder member of the Society for the Advancement of Electrochemical Science and Technology (SAEST). In all the research activities he pursued, his emphasis was on the unification and generalization along with quantitative predictions using simple, mathematical relations.

Tenure at the National Aerospace Laboratory and Indian Institute of Science

As a Homi Bhabha Fellow at the National Aerospace Laboratory, Bangalore, (1970–1975), he was involved in the development of instrumental procedures for the measurement of electrode kinetic parameters. Subsequently, he was invited by Prof Satish Dhawan (then Director of the Indian Institute of Science, Bangalore) to join the Department of Inorganic and Physical Chemistry (IPC). He served as a Professor at the Indian Institute of Science (IISc) till superannuation and inspired PhD students and colleagues of various disciplines, both formally and informally. During his term at IISc, he made extensive contributions pertaining to

electrochemical phase formation, theory of the electrical double layer, quantum chemical theory of electron transfer, linear and non-linear systems analysis, stochastic modeling of electrochemical systems, current distribution at rough geometries, semiconductor-electrolyte interfaces, etc. The essential philosophy underlying his research pursuits during this period was a systematic and hierarchical approach to subtle theoretical questions supported by experimental observations. To him, each research pursuit warranted investigations from different perspectives. His choice of problems was often dictated by the challenges it offered to him. On account of the extensive mathematical repertoire and intuition in his possession, he was able to discover amazingly new results *en route* to solving any problem almost effortlessly! It is hence no wonder that each of his research contributions had a stamp of originality. Even a few days before his demise, he was involved in the formulation of new approaches for current distribution at porous electrodes; he was also planning to deliver a series of lectures at IISc on mathematical modeling of physicochemical systems. On account of his elegant mathematical analysis in conjunction with strict ethical values and principles, he inspired a generation of students and colleagues who hold him in high esteem.

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Return to CECRI

On lien from IISc, he served as the Director of CECRI, Karaikudi between 1988 to 1992. During this brief tenure, he was instrumental in providing a new thrust to the activities of CECRI by holding extensive discussions with various research groups, encompassing all the areas of theoretical and applied electrochemistry. Despite the high demand on his time as a Director, he gave lectures on various topics to the BTech students at CECRI. He had published nearly 200 papers in various journals ranging from the *Journal of Theoretical Biology* to *Journal of Applied Electrochemistry*.

Assignments Abroad

He held various assignments as Visiting Scientist at the Univer-

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sity of Newcastle upon Tyne, Georgetown University, International Centre for Theoretical Physics, IBM Thomas J Watson Research Center, Pennsylvania State University. He was a frequent visitor to different laboratories under the USSR Academy of Sciences and held wide-ranging discussions with the Academician Frumkin. He gave plenary lectures at various International Conferences on Electrochemical Science and Technology.

Honours and Recognitions

SKR was elected as Fellow of the Indian Academy of Sciences, Indian National Science Academy, and the Third World Academy of Sciences. He was in the editorial board of *Electrochimica Acta*. He received the Alumni Award of the Indian Institute of Science, lifetime achievement award of the Chemical Research Society of India and numerous other honours and distinctions. He stood tall among his peers and strode as a colossus in the scientific community. Despite his monumental accomplishments, he remained simple and was always amenable for discussions on a wide range of topics scientific and political.

Hobbies

SKR was a connoisseur of classical music (Carnatic and Hindustani); was a film critic for a Tamil magazine in his early days and *The Four Quartets* by T S Eliot used to be one of his favourite books. He was a voracious reader and was especially fond of English fiction. He used to quote profusely from the poems of Bharathiar and participated actively in various literary events.

Scientific Contributions

The research topics investigated by SKR being extremely diverse, it is truly impossible even to highlight the significant features of each. Hence a glimpse of the contributions on a few selected topics will be given below:

Faradaic Rectification: The redoxo-kinetic method (subsequently christened as Faradaic Rectification) propounded by Doss and

Agarwal in 1951 was a unique technique in that it can be employed for electroanalytical and electrode kinetic studies. Since the rectification voltages are much smaller in comparison with the amplitude of the applied voltage, the theoretical basis and the choice of systems is an essential prerequisite to enlarge the scope of the technique. The rigorous formulation of the theory was elaborately worked out by SKR using an operator algebra[1]. This elegant formalism ensured that the Faradaic rectification became a powerful electrochemical technique with a sound theoretical basis.

[1] *J. Electroanal. Chem.,* Vol.1, p.396, 1959/60.

Accelerated tafel plots for Corrosion Studies: An exponential relaxation method useful in the mechanistic analysis of corrosion phenomena was formulated and applied to a variety of systems[2]. This method became well known in the corrosion literature as the method of accelerated Tafel plots and continues to be widely employed in view of its importance in deducing all the system parameters.

[2] *J. Electroanal.Chem.* Vol.55, p.151, 1974.

Electrochemical Phase Formation: The theory of electrochemical phase formation was one of the favourite topics which engaged his attention continuously. From his first paper on this topic in 1965[3], he continued to focus his attention on various subtle issues such as the effect of multi-component electrocrystallization, and random sequential multilayer deposition till as late as 1994[4]. With extremely clever insights, he developed several time-dependent nucleation and growth models[5]. The diagnostic criteria for distinguishing nucleation-growth mechanisms from the experimental current transients were developed[6]. These results have been widely employed in the electrochemical phase formation.

[3] *Can. J. Chem.,* Vol.43, p.1052, 1965.

[4] *J. Electroanal. Chem.* Vol.66, p.271, 1994.

[5] *J. Chem. Soc. Faraday Transactions* I, Vol.77, p.483, 1981.

[6] *J. Electroanal. Chem.,* Vol.134, p.225, 1982.

Systems Analysis: During his tenure at NAL Bangalore as a Homi Bhabha Fellow, he developed the systems analysis for electrochemical systems[7] by defining a new operator called 'm-operator' ('m' denoting the mass transfer). This approach is so general that it can be applied to any mode of mass transfer (diffusion, migration, convection) and any electrochemical

[7] *J. Electroanal. Chem.,* Vol.41, pp.459, 473, 491, 1973.

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mechanism (Butler--Volmer, Tafel), any type of perturbation (linear, sinusoidal, etc), any modes of adsorption (Langmuir, Frumkin, Freundlich, Temkin) in conjunction with coupling between various phenomena. In fact, it will not be an exaggeration to mention that the theory behind all electrochemical techniques including the now popular cyclic voltammetry, impedance spectroscopy, is embedded in this series of papers. The major breakthrough in this analysis has been the representation of the concentration fluctuations of the reactant and product in terms of the current using matrix algebra. One may note that deducing the surface concentrations of the species from the transient electrochemical data remains an unsolved problem even today!

Electrical Double Layer Theories: The analysis of adsorption phenomena (ions, solvent dipoles, organic compounds) at the electrochemical interfaces has been a fascinating topic for him ever since his discussions with the Academician Frumkin. By writing the Gibbs free energy of adsorption as an analytic and non-analytic part in surface coverage, he was able to generalize almost all the known isotherms (Henry, Langmuir,Volmer, HFL,Virial, Frumkin, Hill–de Boer, Parsons, Temkin, Blomgren–Bockris, etc.)[8]. The choice of electrical variable in adsorption and a novel method of deducing the two-dimensional equation of state from the adsorption isotherms was postulated[9]. By employing an Ising model description, he was able to generalize adsorption isotherms pertaining to diverse classes of compounds. With the help of clever statistical mechanical modeling in conjunction with incorporation of interfacial interactions, a hierarchy of adsorption isotherms was proposed[10].

Many Body Theory and Electron Transfer Formalism: Commencing from the late seventies and till early nineties, SKR focused his attention on quantum electrochemistry encompassing the theory of electron transfer at electrode surfaces and chemisorption phenomena. The superoperator formalism was employed for chemisorption for different types of Hamiltonians and elegant solutions were obtained for different experimental observables[11]. Employing the Anderson--Newns Hamiltonian, the electronic

[8] *J. Electroanal. Chem.,* Vol.45, p.283, 1973.

[9] *J. Electroanal. Chem.* Vol.57, p.1, 1975.

[10] *J. Electroanal. Chem.*, Vol.176, pp.1, 29, 45, 65, 99, 119, 1984.

[11] *Mol.Phys.,* Vol.38, p.1567, 1979.

density of states were computed and the implications regarding the experimental data pointed out[12].

Modelling of Roughness: The effect of surface roughness on the diffusion-limited current density in electrochemical techniques was investigated with special reference to interfacial admittance[13]. The inverse problem of extracting the roughness of electrodes from the experimental observables was a recurrent theme in several of his subsequent papers too.

Impedance Spectroscopy: He made significant contributions to the analysis of impedance data pertaining to complex systems and geometries; in particular, he decoded the signature of various processes (double layer capacitance, charge transfer resistance, constant phase elements, etc.) in the experimental impedance data (Nyquist plots, Bode plots, etc.). These analyses warranted expertise in solution of non-linear partial differential equations, circuit theory, integral transforms and Green's functions. The crucial role played by the geometry of the electrodes in the interpretation of the impedance data has been repeatedly emphasized. The analysis of impedance techniques pertaining to porous electrodes[14], electrode kinetics[15], bilayer lipid membranes[16], Ru/Ti oxide electrodes[17], etc., has engaged his attention continuously.

Pade' Approximants: The extreme versatility of Pade approximants and other rational function approximations to the study of chronopotentiometry[18] , virial equation of state, phase transitions and critical phenomena[19] was pointed out with a variety of new examples. An entirely novel Bessel function identity pertaining to all types of polynomials was proposed and its significance in solving several statistical mechanical models was pointed out[20].

Special functions and Mathematical Analysis: He has repeatedly emphasized the 'un-reasonable effectiveness of mathematics' in a variety of physicochemical situations. Despite his basic degree in Mathematics, his first publication pertained to the

[12] *J. Phys. Che*m., Vol.91, p.3406, 3417, 3425, 1987.

[13] *J. Electroanal. Chem.*, Vol.396, p.285,1995.

[14] *J. Electroanal. Chem.*, Vol.22, p.89, 1969.

[15] *J. Electroanal. Chem.,* Vol.324,pp.405, 1992. Vol.552, p.151, 2003.

[16] *J. Electroanal. Chem.,* Vol.100, p.33, 1979.

[17] *J. Electrochemical Society,* Vol.148, D112, 2001.

[18] *J. Electroanal. Chem.,* Vol.265, p.35, 1989.

[19] *Chem. Phys. Lett.*, Vol.101, p.49, 1983.

[20] *Phys. Lett.,* Vol.A96, p.339, 1983.

interpretation of the Faradaic Rectification a problem in electrochemistry posed by his mentor, KSG Doss. In chronological order, his fifth publication dealt with the Laguerre polynomials[21]. Ironically, his final publication was on Lanczos' generalized derivatives[22]. During the intervening four decades, he has made original contributions in special functions, stochastic modeling, kinetic Ising models, perturbation expansions, Appell polynomials, etc.

[21] *Proc Indian Academy of Sciences,* Vol.58, p.362, 1963.

[22] *J. Computational and Applied Mathematics,* Vol.177, p.461, 2005.

Miscellaneous Topics: The range of miscellaneous topics is so diverse that it is difficult to list each one of them; suffice to point out a few topics in applied electrochemistry in order to illustrate his constant touch with industrial and experimental electrochemistry viz. current distribution in bipolar cells, semiconductor electrochemistry, supercapacitors, lead acid battery.

Although the above provides a brief outline of a few of his contributions, his *tour de force* consisted in the quantification of any phenomenon in mathematical language, from diverse perspectives. His approach was 'not to dismiss' any experimental observations; in fact he had a penchant for 'anomalous' behavior. He could generate entirely new results in pure mathematics as and when required. His clarity in thought coupled with his phenomenal expertise in all branches of physics and mathematics ensured that any problem posed to him was solved almost instantaneously.

Rangarajan was a mentor and guru for a large number of students and colleagues. His elegant mathematical insights coupled with humane, sympathetic approach endeared everyone who came into contact with him. In his death, the scientific community has not only lost a true genius but also a kind, passionate human being –deviod of any human weakness. Despite his mortal death, the moral and scientific values instilled by him will remain eternally in memory for his family of students, colleagues and admirers all over the world.

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