

With the status of current secondary and tertiary services being as briefly stated above, the innovative approach of the *Solubility Data Project* is that its compilation and critical evaluation work involve consolidation and reprocessing services when both activities are based on intellectual and scholarly reworking of information from primary sources. It comprises compact compilation, rationalization and simplification, and the fitting of isolated numerical data into a critically evaluated general framework.

The *Solubility Data Project* has developed a mechanism which involves a number of innovations in exploiting the literature fully, and which contains new elements of a more imaginative approach for transfer of reliable information from primary to secondary/tertiary sources. *The fundamental trend of the Solubility Data Project is toward integration of secondary and tertiary services with the objective of producing in-depth critical analysis and evaluation which are characteristic to secondary services, in a scope as broad as conventional tertiary services.*

Fundamental to the philosophy of the project is the recognition that the basic element of strength is the active participation of career scientists in it. Consolidating primary data, producing a truly critically-evaluated set of numerical data, and synthesizing data in a meaningful relationship are demands considered worthy of the efforts of top scientists. Career scientists, who themselves contribute to science by their involvement in active scientific research, are the backbone of the project. The scholarly work is commissioned to recognized authorities, involving a process of careful selection in the best tradition of IUPAC. This selection in turn is the key to the quality of the output. These top experts are expected to view their specific topics dispassionately, paying equal attention to their own contributions and to those of their peers. They digest literature data into a coherent story by weeding out what is wrong from what is believed to be right. To fulfill this task, the evaluator must cover all relevant open literature. No reference is excluded by design and every effort is made to detect every bit of relevant primary source. Poor quality or wrong data are mentioned and explicitly disqualified as such. In fact, it is only when the reliable data are presented alongside the unreliable data that proper justice can be done. The user is bound to have incomparably more confidence in a succinct evaluative commentary and a comprehensive review with a complete bibliography to both good and poor data.

It is the standard practice that the treatment of any given solute-solvent system consists of two essential parts: I. Critical Evaluation and Recommended Values, and II. Compiled Data Sheets.

The Critical Evaluation part gives the following information:

- (i) a verbal text of evaluation which discusses the numerical solubility information appearing in the primary sources located in the literature. The evaluation text concerns primarily the quality of data after consideration of the purity of the materials and their characterization, the experimental method employed and the uncertainties in control of physical parameters, the reproducibility of the data, the agreement of the worker's results on accepted test systems with standard values, and finally, the fitting of data, with suitable statistical tests, to mathematical functions;
- (ii) a set of recommended numerical data. Whenever possible, the set of recommended data includes weighted average and standard deviations, and a set of smoothing equations derived from the experimental data endorsed by the evaluator;
- (iii) a graphical plot of recommended data.

The Compilation part consists of data sheets of the best experimental data in the primary literature. Generally speaking, such independent data sheets are given only to the best and endorsed data covering the known range of experimental parameters. Data sheets based on primary sources where the data are of a lower precision are given only when no better data are available. Experimental data with a precision poorer than considered acceptable are reproduced in the form of data sheets when they are the only known data for a particular system. Such data are considered to be still suitable for some applications, and their presence in the compilation should alert researchers to areas that need more work.

The typical data sheet carries the following information:

- (i) components - definition of the system - their names, formulas and Chemical Abstracts registry numbers;
- (ii) reference to the primary source where the numerical information is reported. In cases when the primary source is a less common periodical or a report document, published though of limited availability, abstract references are also given;
- (iii) experimental variables;
- (iv) identification of the compiler;
- (v) experimental values as they appear in the primary source. Whenever available, the data may be given both in tabular and graphical form. If auxiliary information is available, the experimental data are converted also to SI units by the compiler.

Under the general heading of Auxiliary Information, the essential experimental details are summarized:

- (vi) experimental method used for the generation of data;
- (vii) type of apparatus and procedure employed;
- (viii) source and purity of materials;
- (ix) estimated error;
- (x) references relevant to the generation of experimental data as cited in the primary source.

This new approach to numerical data presentation, formulated at the initiation of the project and perfected as experience has accumulated, has been strongly influenced by the diversity of background of those whom we are supposed to serve. We thus deemed it right to preface the evaluation/compilation sheets in each volume with a detailed discussion of the principles of the accurate determination of relevant solubility data and related thermodynamic information.

Finally, the role of education is more than corollary to the efforts we are seeking. The scientific standards advocated here are necessary to strengthen science and technology, and should be regarded as a major effort in the training and formation of the next generation of scientists and engineers. Specifically, we believe that there is going to be an impact of our project on scientific-communication practices. The quality of consolidation adopted by this program offers down-to-earth guidelines, concrete examples which are bound to make primary publication services more responsive than ever before to the needs of users. The self-regulatory message to scientists of the early 1970s to refrain from unnecessary publication has not achieved much. A good fraction of the literature is still cluttered with poor-quality articles. The Weinberg report (in 'Reader in Science Information', ed. J. Sherrod and A. Hodina, Microcard Editions Books, Indian Head, Inc., 1973, p. 292) states that 'admonition to authors to restrain themselves from premature, unnecessary publication can have little effect unless the climate of the entire technical and scholarly community encourages restraint...' We think that projects of this kind translate the climate into operational terms by exerting pressure on authors to avoid submitting low-grade material. The type of our output, we hope, will encourage attention to quality as authors will increasingly realize that their work will not be suited for permanent retrievability unless it meets the standards adopted in this project. It should help to dispel confusion in the minds of many authors of what represents a permanently useful bit of information of an archival value, and what does not.

If we succeed in that aim, even partially, we have then done our share in protecting the scientific community from unwanted and irrelevant, wrong numerical information.

A. S. Kertes

PREFACE

SCOPE OF THE VOLUME

This volume deals with the solubilities of the halides of scandium, yttrium, lanthanum, and lanthanides in nonaqueous solvents. The volume includes the solubilities of these "rare earth" halides in both organic and inorganic solvents, and in mixed solvents containing water where water is the minor constituent of the mixed solvent. The solubilities of rare earth halides in mixed water-organic solvents covering the entire composition range of 100 % water to 100 % organic component will be published in a forthcoming volume.

The literature on the solubilities of Sc, Y, La and the lanthanide halides in nonaqueous solvents has been covered through 1984, and only a few systems have not been compiled. The paper by Safonov et al. (1) dealing with the solubility of NdCl_3 in SeOCl_2 and POCl_3 has been rejected since it contains only qualitative limits of solubilities. Similarly we have rejected the data of Nikolaev et al. (2) who reported the solubilities of rare earth fluorides in water and liquid HF: the results were presented graphically. Data from (3) have also been omitted since the original data were reported in other publications which have been compiled in this volume. It is also noted that solubility data for *didymium chloride* in a number of ethers (4) have been rejected since didymium is a mixture of rare earths.

Most of the solubility data reported in the literature are either in mass % units or in units of mol kg^{-1} . A number of *Masters Theses* originating in the laboratory of Prof. Hopkins (University of Illinois) around 1930-1934 report solubilities in mol dm^{-3} units. Since density data are generally unavailable, direct comparisons of these early data with more recent results based on mass units are not possible. Hence we have not prepared critical evaluations for those systems for which two publications exist, and for which one publication reports solubilities in volume units and the other in mass units.

NATURE OF THE SOLID PHASE

For those researches which report analyses of equilibrated solid phases, we find considerable disagreement in the reported compositions. For example at 298.2 K Grigorovich (5) reports a solid phase of $\text{NdCl}_3 \cdot 3\text{CH}_3\text{OH}$ as opposed to $\text{NdCl}_3 \cdot 4\text{CH}_3\text{OH}$ reported by Merbach et al. (6). Since Grigorovich's solubility data are always significantly greater than those of all other workers, the evaluators assumed that Grigorovich's results might be based upon metastable equilibria. However it is always possible that errors exist in analyses of the solid phases which have escaped detection by the evaluators because of insufficient experimental descriptions in the source publications. Grigorovich's high solubilities could be due to a constant error in calculation. For example he reports a solubility of 32.04 mass % for PrCl_3 in 1-propanol at 298.2 K, and assuming this result to be based on the *anhydrous* PrCl_3 the evaluators calculated a solubility of 1.91 mol kg^{-1} . However if the solubility of 32.04 mass % is based on the solvate $\text{PrCl}_3 \cdot 2\text{C}_3\text{H}_7\text{OH}$, then the solubility calculated by the editors is 1.28 mol kg^{-1} which is close to the result of 1.24 mol kg^{-1} reported by Kirmse (7): note that Kirmse reports the solid phase to be $\text{PrCl}_3 \cdot \text{C}_3\text{H}_7\text{OH}$. Although all of Grigorovich's mass % results have been *assumed* by the evaluators to be based on the anhydrous salts, the reader should be aware that there is a high probability that Grigorovich's data are based upon mass % of the solvate, and that the reported compositions of the solvates may also be in error.

GENERAL COMMENTS

A major part of this volume consists of compilations from publications of Prof. E.M. Kirmse and her colleagues (in particular H. Dressler). Due to the fact that experimental details in Prof. Kirmse's publications are often incomplete, and due to the fact that her works form a principal part of this volume, it seems appropriate to combine the experimental details from all of her publications and present them in one place. The following therefore is a combined review of Prof. Kirmse's experimental techniques.

"Anhydrous salts were prepared from the oxide or directly from the halide by the method of Taylor and Carter. Saturated solutions were prepared isothermally by mechanical agitation either by thermostating at $298 \pm 0.2 \text{ K}$ or at room temperature (291-298 K). Aliquots of saturated solution were treated with KOH solution to precipitate the rare earth hydroxide, and the rare earth content determined by complexometric titration. In several instances (e.g. with fluorides) the anion concentration was also determined. Anhydrous reagents were handled in a dry box containing P_2O_5 , and the reported solubilities are mean values of 2-4 determinations. Solid phases were analysed from "wet" residues which were placed in a vacuum desiccator over P_2O_5 until constant mass was obtained. Both the rare earth content and the anion content of the solid phases were determined."

Noticeably absent in all of Prof. Kirmse's publications are the sources and purities of starting materials (oxides, halides, solvents). It is not clear why the rare earth fluorides prepared by Kirmse and Dressler by the wet method are not stoichiometric. It would appear that in spite of heating at around 580 K for 120 days, they obtained partially hydrated salts.

We conclude that the determination of the solubilities of anhydrous rare earth halides is subject to many sources of error. In spite of the large amount of data reported, significant disagreement exists, particularly with respect to composition of the solid phases. More rigorous thermodynamic treatment of these solubility data requires an exact knowledge of the compositions of the solid phases, and a precise determination of both stable and metastable equilibria. We hope that the present volume will serve as a useful guide in this respect.

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