LIQUID-LIQUID SOLUBILITY: EVALUATION PHILOSOPHY AND METHODOLOGY
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INTRODUCTION

Because of the differing ways in which it is possible to critically evaluate published solubility data it is worthwhile to present a coherent statement on the philosophy and procedures which have been used in this volume. Although this is a personal statement concerning the present volume, many of the ideas have been developed by myself as an evaluator for previous liquid-liquid volumes in the Solubility Data Series [1-3] and are shared, to some degree, by other evaluators.

EVALUATION PHILOSOPHY

The critical evaluation of data is, at least in part, a subjective process. Some physical scientists are uncomfortable with this notion but the history of science shows us it is undeniable. Because some subjective judgements are inevitably involved, it is vital that the evaluator's procedure should be as visible as possible. In this way, if the user does not agree with the evaluator's judgement or arguments or if new data become available it is possible, with a minimum of effort, to derive a new set of preferred or "best" values. For this reason the Critical Evaluations in this and those previous volumes to which I have contributed [1-3] have been, in essence, written like research papers with enough information provided for users to repeat or change the evaluation should they so desire.

The starting point for each Critical Evaluation is that the data compilation is complete, i.e., the data sheets include all the available data. This is an important premise because the addition of extra data may change the evaluation considerably. This is especially true of liquid-liquid systems since very few have been adequately studied over a wide temperature range and disagreements often exist between independent investigations.

In general, a "democracy of observers" is followed. That is, the data of all investigators are given equal weight irrespective of their reputation or location. This is justifiable in scientific terms because experience shows that real "errors" in liquid-liquid solubility data are much greater than individual authors' reported precisions. Thus, the benzene-water system, which is relatively simple and probably the most widely studied of all liquid-liquid systems [3], has solubilities which are known to an accuracy of about ± 2% (relative). The same estimated error is obtained regardless of whether a simple average of the available data is taken or whether a complex weighting procedure is used. This suggests that, at the present stage of development of liquid-liquid solubility determinations, equal weighting for all data is the most appropriate course of action. The exceptions to this rule are discussed below.

REJECTION OF DATA

The statement that all data are given equal weight must be qualified: some data are assigned zero weight, i.e., they are rejected. Data rejection is potentially dangerous, especially when few data are available. Nevertheless, since a critical evaluation is required, it has to be considered. The most important reasons for rejecting data are as follows.

1. The data disagree "significantly" from most other studies (especially if these are numerous). Significance is subjective but a criterion of

   \[ |s_{\text{obs}} - s_{\text{av}}| > 3s_n \]

   where \( s_{\text{obs}} \) is the reported solubility datum being considered for rejection,
   \( s_{\text{av}} \) is the arithmetic average (mean) of all other studies at the same temperature and pressure,
   \( s_n \) is the standard deviation from the mean of these studies has been generally, but not rigidly, applied [1-3].

It should be noted that this procedure can be invoked only once. That is, having rejected some points in a particular data set it is not statistically valid to recalculate a new value of $\sigma$ and then reject further points. Strictly speaking this means that outlying data should be included in the original calculation of $\sigma$. However, the amount of available data does not always make this approach realistic and common sense must be applied.

2. Approximate data (one significant figure) are rejected when a reasonable amount of more precise data is available.

3. Data which are grossly inconsistent with chemical systematics or thermodynamic expectations are also rejected.

4. In keeping with the practice adopted in previous liquid-liquid solubility values, data originally presented in graphical form or in volume ratio units are also excluded. In the latter case, data are retained if appropriate density data are readily available to permit conversion to mass units. As density measurements are usually far more reliable than solubility data, the choice of density values is usually not critical.

It is appropriate to add here that data for a particular system coming from the same authors or the same laboratories have generally not been regarded as independent measurements and have therefore been subsumed into a single result (at each temperature).

THE EVALUATION FORMAT

The Critical Evaluations in this volume follow the format evolved in previous liquid-liquid solubility volumes [1-3]. In essence each Evaluation is divided into three parts. In the first part Table 1 lists all the available publications containing quantitative solubility data for the particular system. Broad experimental details such as temperature range, type of solubility measured ((1) in (2), (2) in (1) or mutual) and the method used are also included in Table 1. After mention of any other special features such as critical points, or any special types of investigation, further discussion is usually divided into two parts: the solubility of the organic in the aqueous phase, and that of water in the organic-rich phase. Since these two sections are handled in the same way they will be discussed together.

After listing rejected data, anomalies and caveats, all the available data (usually expressed as g/100g sln) are collected into Tables (usually Tables 2 & 3). To facilitate comparisons, data are interpolated (if necessary) to specific temperatures at 5K intervals near 298K, then 10 or 20K intervals. These temperatures are exact, i.e. 298.15, 303.15 ... K but for convenience are written 298, 303, ... K in the text. The nature of most liquid-liquid solubility data makes graphical interpolation the most appropriate approach [4]. Interpolated values are always designated with an asterisk (*). Very occasionally data are extrapolated but only over a short range (<5K) and only if the solubility curve is not changing sharply.

All the retained values at each temperature are then averaged and the mean and $\sigma$ recorded in the Tables. Few of the systems in this volume have sufficient data to permit meaningful statistical analysis. The value of $\sigma$ is therefore included only as a convenient measure of the spread of the experimental data.

"BEST" VALUES

The word "best", almost always in inverted commas (quotation marks), is used throughout the Critical Evaluations in this and previous liquid-liquid solubility volumes [1-3] in a specific way: to mean "best available estimate". It follows from what has been said above that "best" values are simply the arithmetic average (mean) of all the accepted data, including those obtained by interpolation and excluding rejected data. "Best" values are given in both g/100g sln and mole fraction units (x).
RECOMMENDED VALUES

Solubilities are recommended only if two or more independent studies (including rejected data) agree to within ±5% (relative), i.e.,

$$|100\sigma_n/\langle x_n\rangle| \leq 5$$

and there are no other obvious problems. Recommended data are designated by (R) immediately following the numerical value.

For sparingly soluble systems this criterion may be too harsh and

$$|100\sigma_n/\langle x_n\rangle| \leq 10 \text{ or } 20$$

may be more appropriate [3]. Very few high molecular weight esters have been sufficiently well characterized to enable even these less restrictive criteria to be applied.

Data which are not "Recommended" are regarded as "Tentative". The likely accuracy of these data varies from system to system and from temperature to temperature but may be inferred from

1. $$\sigma_n$$
2. $$100\sigma_n/\langle x_n\rangle$$
3. n (the number of independent measurements).

Occasionally there are definite reasons to suspect the available data are not reliable. Such data are labelled "Doubtful" and the detailed reasons for this classification given. Considerable care should be exercised in the use of such data.

Note that the mole fraction "best" solubilities in each table should be regarded as having the same status ("Recommended", "Tentative" or "Doubtful") and the same (relative) percentage uncertainties (where given) as the corresponding mass % solubilities.

GRAPHICS

In systems for which a reasonable amount of data exists, selected results are plotted graphically over the studied temperature range. Appropriate comments on the plots are made in the figure caption or in the text.

FITTING EQUATIONS

The use of fitting equations to smooth solubility data as a function of temperature is controversial and a topic in its own right which will not be discussed here. As in previous liquid-liquid solubility volumes [1-3], fitting equations are not generally given in the printed version of this volume. There are several reasons for this.

1. There is no single equation form which can be used for all systems.
2. The data for some systems are too scattered or poorly defined for realistic curve fitting.
3. Without special care empirical fitting equations may give misleading results (spurious extrema, etc.) when interpolating and can almost never be reliably used for extrapolation.

For certain systems where reliable data appear evident, fitting equations have been provided. Such equations come directly from the original works or from the efforts of the compilers in the course of their examination of reported data and preparation of smoothed value tables.

Users who wish to derive their own fitting equations are advised to do so with caution. It is suggested that the "best" values be used for this purpose, but it should be noted that this may create anomalies because of the way in which the "best" values are derived (see above). Where fitting equations are given in this volume they should be used only over the stated range.
THERMODYNAMIC CONSISTENCY

Using standard relationships from thermodynamics it can be shown that:

\[ \Delta_{\text{gln}C} = -RT \ln a_{\text{sat}} \]

\[ \frac{\partial (\Delta_{\text{gln}C}/T)}{\partial T} = -\frac{\Delta_{\text{gln}H}}{RT^2} \]

and

\[ \frac{\partial^2 (\Delta_{\text{gln}C}/T)}{\partial T^2} = \frac{\partial (\Delta_{\text{gln}H})}{\partial T} = \Delta_{\text{gln}C_P} \]

where \( \Delta_{\text{gln}C} \), \( \Delta_{\text{gln}H} \) and \( \Delta_{\text{gln}C_P} \) are respectively the Gibbs energy, enthalpy and heat capacity (at constant pressure) changes corresponding to the dissolution of the solute in the solvent and \( a_{\text{sat}} \) is the activity of the saturated solute in the solvent. If the solute is only sparingly soluble the thermodynamic parameters may be equated with their standard state values, and it should be noted that \( \Delta_{\text{gln}C_P} \) may itself be temperature dependent.

Both \( \Delta_{\text{gln}H} \) and \( \Delta_{\text{gln}C_P} \), at least in principle, can be measured directly by separate calorimetric procedures \(^{[5,6]}\) and therefore can serve as an independent check on the temperature dependence of published solubility data. This approach has been used with significant effect in evaluating hydrocarbon solubilities in water \(^{[2-3]}\). However, very few calorimetric data have been reported for ester-water systems and so this approach has not been utilized in the present volume.

REFERENCES


