

# THE LAW OF MASS-ACTION VERSUS NON-IDEAL BEHAVIOUR IN DISTRIBUTION EQUILIBRIA

Y. MARGUS

*Department of Inorganic and Analytical Chemistry, The Hebrew University,  
Jerusalem*

The necessity of preparing this talk at very short notice does not permit me in this plenary lecture to present original material or to advance the frontiers of the science of solvent extraction. It does, however, give me the opportunity to ask: what are we solvent extraction chemists doing? There are, of course, the fortunate among us whose occupation is to separate things by extraction. They have a simple criterion for measuring their success, which is by noting whether they have, indeed, achieved the required separation to a sufficient degree. If furthermore, they investigate an industrial process, they have the additional criterion of whether their process is economical or not.

Those others amongst us, who care for the physical chemistry of distribution equilibria, have different problems, and it is more difficult for them to define their goals. At the 4th ICSEC in Gothenburg, Lars Gunnar Sillén proposed the objective of looking for the identity of the species swimming around in our solutions and their relative amounts<sup>1</sup>. Let us consider and see whether we are successful in this task.

There are two general approaches to the problem of finding out what are the species swimming around in the solutions. In one of them we measure some physical property of the solution, and relate it to the possible species present. It is somewhat easier when we can measure a property directly connected with the nature of the species we are looking for, and preferably proportional to its concentration, such as the intensity of a Raman line. Often we measure only a gross property, characteristic of the solution as a whole, and have to interpret it in terms of the separate properties of the solvent and the solute or solutes. We may be successful in this, and find what we are looking for, that is the nature of the species in solution. To find their relative amounts, however, we almost always invoke the law of mass-action, in a procedure similar to that employed in the second general approach, to be mentioned now.

In this second approach, we utilize the fact that in distribution equilibria we have two phases and generally sufficient degrees of freedom within which the compositions of the phases vary, but in a related way. Thus, we measure the gross distribution coefficient of a given solute of interest, and relate it to the composition of the phases. From an appropriate analysis of these data, we then find both the species present and their relative concentrations, again using the law of mass action. One popular method of interpreting the data, which provides the basis for design of the experiments, is slope analysis.

This is quite a legitimate method, provided the necessary precautions are taken to do it properly. However, and this is the central weakness of the whole procedure as I see it, we rarely do it properly, since the apparent simplicity of performing these experiments and doing the slope analysis fools us into accepting the results without too many questions. The same is true for other methods involving distribution data and the law of mass-action.

We should thus examine our methods critically, so that we can dispose of their implicit assumptions, replace some of them with definite statements based on proven facts, and make the necessarily remaining ones explicit. These can then be proven or disproven later, when better methods and more knowledge are available.

Since such general exhortations have been made repeatedly by others, it is appropriate now to come down to earth and give specific examples.

Let us consider the monobasic dialkylphosphoric acid esters. There is general agreement that these are dimeric in solutions in hydrocarbon or halocarbon diluents, and a simple structural formula can be drawn for the dimer. But what is the experimental evidence for the presence of these dimers? Several cryoscopic, isopiestic vapour pressure, distribution coefficient and n.m.r. measurements consistently give molecular weights for the species in solution near, but systematically up to 20 per cent higher than that of the dimer<sup>2</sup>. Are we then correct in concluding that there are larger aggregates present to a certain extent? Some distribution studies of metal ions with these extractants, have indeed been interpreted in terms of dialkylphosphate trimers being the major extracting species in a certain concentration range. However, in other studies, these extractants in the same concentration range and in the same diluent still acted as dimers, in extraction of certain other metal ions.

The uncertainties are increased with another acidic extractant: dinonylnaphthalene sulphonate (DNNS). The distribution coefficients for tracer metals depend on the first power of the extractant concentration over a wide range of concentrations, and irrespective of the charge of the metal ion.<sup>3</sup> This is interpreted as indicating extraction by a large aggregate, into which the metal ions are incorporated. A similar extractant, dodecylbenzene sulphonic acid shows, however, a second power dependence<sup>3</sup>. Both extractants are indeed aggregated in solution, and approximately to a similar degree, but certainly not to such a large extent as is consistent with the interpretation of the DNNS data. Information independent of the distribution measurements shows *ca.* 10 monomer units present per aggregate. This relatively small size should be reflected in the concentration dependence by a deviation from a uniform slope, but this is not the case.

Let us now turn to quite a different class of extractants, acting not by compound formation but by solvation. A well known example of distribution data not behaving according to simple expectation is the extraction of metal chloride complexes from aqueous hydrochloric acid with diethyl ether. As the hydrochloric acid concentration increases beyond *ca.* 7M in the aqueous phase, the distribution coefficient for, say, gallium chloride decreases.<sup>4</sup> Independent evidence, obtainable by many different methods, even including distribution data (with  $\beta, \beta'$  dichloro diethyl ether), show

that no new gallium species are formed beyond 7M HCl in aqueous solutions. The point here is, of course, that what we have considered to be the aqueous phase is no longer an aqueous solution beyond 7M HCl, but a water-rich ether solution, and that indeed new species are formed in this phase—ether solvated hydrated protons associated with tetrachlorogallate ions. These show a quite different distribution behavior between the two phases—water rich and water poor ether, respectively, which are not at all like those present at low hydrochloric acid molarities. In this case it is not a failure due to the high concentration of hydrochloric acid—7M—since other extractants give perfectly valid results. It is a failure of the extractant we have used, and of a basic assumption which we have made—that of mutual immiscibility of the two phases.

The next example we may consider is that of the hydration of tributylphosphate (TBP). At room temperature, TBP in equilibrium with water has the approximate composition 3.6 M TBP and 3.6 M H<sub>2</sub>O. Is it then correct to conclude from the stoichiometry that a stable monohydrate is formed in this system? We now know that this conclusion is incorrect, since by somewhat changing the temperature or the water activity, quite different ratios of H<sub>2</sub>O:TBP are obtained in the equilibrium solution<sup>5</sup>. Should we then conclude that no 1:1 hydrate is formed in this system? This is also too far reaching, since there is good infrared spectral evidence that hydration does occur—thus not only mere solubility—and this, together with n.m.r., dielectric constant, enthalpy of solution and distribution data show that a 1:1 hydrate is formed, being one species in a series of other hydrates, along with molecules of TBP interacting with TBP, and those of water interacting with water, rather than mutually.

Considering now a third class of extraction systems—that involving ion association with, say, long-chain alkyl substituted ammonium cations—we come up against similar problems. We know that these salts are aggregated, and cryoscopic measurements indeed show the formation of octamers in solutions of up to 0.5M trialkyl ammine hydrohalide salts in benzene. We expect aggregation to increase with increasing concentration, but the data show us unambiguously that this is not so, the average aggregation number decreasing to two, as the amine salt concentration increases beyond 1M. This finding of decreasing aggregation with increasing concentration is corroborated also by acid extraction data.<sup>6</sup> The apparent failure of the law of mass-action in this case is connected with gross changes in the nature of the solution from predominantly non-polar to rather polar as the concentration changes in the above-mentioned range, with the concomitant effects on the aggregation.

For a final example, we shall cite the remarkable metal extraction behaviour evidenced by these long-chain ammonium salt extractants. From a large array of methods, we know that their aggregates in the usual diluents used, such as aromatic hydrocarbons, are not large clusters but rather oligomers of two to eight members each<sup>7</sup>. In the concentration range used for metal complex extraction, say 0.01–0.2 M, these aggregation equilibria therefore gradually shift. Thus, the dependence of the distribution coefficient of the metal on the total ammonium salt concentration should be rather complicated. However, this is not the case. Often good first or second power

dependences are found for a wide concentration range, notwithstanding the changes in the extracting species. Mass-action law equations cannot be written to explain this behaviour, not even highly artificial ones involving rather unlikely processes.

When we now consider the apparent failure of the law of mass-action, we prefer not to lose our faith in thermodynamics. We may go back to first principles, and look at the chemical potentials of the components of a mixture at equilibrium. We then see that the chemical potential depends, at a given temperature and pressure, on the concentration of a species which interests us, not only via a  $RT \ln C$  term, but also through several others, including electrical interaction terms, dipole interaction terms, effects on solvent structure, entropy of mixing terms, and so on.

Now, as far as dilute aqueous solutions are concerned, we have achieved a good degree of sophistication in handling these contributions to the chemical potential of a solute. We also have empirical methods for dealing with non-dilute aqueous solutions. From experience we are reasonably confident that we can keep all the terms except  $RT \ln C$  constant, when we change  $C$  within certain limits, provided that we take certain precautions, such as working in a constant ionic medium. Alternatively, we have means of estimating the change in the other terms, as  $C$  varies, so that we can take them into account. Is this the case also for the organic solutions of our extractants? Of course not, as we all know but often fail to consider, and there are two major reasons, which we shall now discuss.

The first, which has perhaps not been given due regard, is the large difference in the molar weight and volume of water on the one hand and of organic solvents and diluents on the other. One kg or one litre of water contains *ca.* 55 moles, and even a 0.5 M solution of an electrolyte is—apart from electrical interactions—a dilute solution, with 100 moles of solvent per mole of electrolyte, so that even with considerable solvation of the dissociated ions, there is still plenty of free solvent to form a continuum in which the ions move.

With a water-immiscible organic solvent the situation is quite different, there being perhaps only 3–10 moles of solvent per kg or per litre. Furthermore, the solutes involved have large molar volumes (*e.g.* 273 ml for TBP, *ca.* 450 ml for trioctylamine hydrochloride), so that even with a 0.5M solution a very appreciable fraction of the volume is occupied by the solute. There are then only a few solvent molecules to surround each solute molecule and interact with it, so that the diluent may perhaps not form a continuum.

This point is of particular importance in the entropy of mixing term, when applied to the organic phase. An undecided question in the thermodynamics of mixtures is whether ideal mixtures should be defined in terms of mole fractions or of volume fractions. Apart from any problem introduced by interactions, an extractant-diluent system which is ideal on the one scale cannot be ideal on the other when, as usual, the molar volumes are considerably different.<sup>8</sup> For the sake of precision, let us define ideality on the mole-fraction scale, and see what deviations are involved.

Consider a distribution system which is ideal, thus:

$$D_{I(x)} \neq f(x_1) \quad (1)$$

where  $I$  is the distribuend. If we now calculate the ordinary distribution coefficient, that is using the molar scale, we obtain

$$D_{I(C)} = D_{I(x)} \frac{1000/V_S' + C_I' (1 - V_I/V_S')}{1000/V_S'' + C_I'' (1 - V_I/V_S'')} \quad (2)$$

where  $S$  is the solvent,  $V$ 's are molar volumes and primes denote the phases. For a typical case of  $V_S'' = 18$  (for water),  $V_S' = 180$  and  $V_I = 90$  we obtain for a constant  $D_{I(x)} = 10$  varying values of  $D_{I(C)}$ , deviating about 20 percent at  $C_I'' = 1M$ , and much more at higher concentrations. With more extreme variation in size of the distribuend and the two solvents (one of them being water), the deviations can be very appreciable even for the ideal case of there being no interactions.

The other reason why non-idealities become more serious in organic solvents than in water is much better recognized—it is the enhanced electrostatic interaction due to the lower dielectric constant. If we want to apply the Debye-Hückel theory for electrolytes, we should observe the limit  $\kappa a < 0.2$ , which can be written as  $C < 2 \times 10^{-4}\epsilon$  for 1:1 electrolytes, where  $C$ , however, refers to the ionic part of the solute. For completely dissociated electrolytes, then, the limit in organic solvents is as much below the practical limit of *ca.* 0.05 M in water, as is the dielectric constant. In the organic solvents, however, association is of great importance, and we must then ask whether the associates are polar or not, and if they are, how important dipole interactions become in these solutions. Unfortunately, we cannot give satisfactory answers to these questions. Although conductivities can be rather low in solvents of dielectric constant of *ca.* 10 (possibly made up of a non-polar diluent and a polar extractant), indicating extensive association, the ion pairs formed will often be constituted from bulky ions, leading to a high dipole moment. The mutual interaction of these dipoles, and their interactions with polarized solvent molecules will be important in organic solvents even at high dilution, because of the long range of the electrical forces in low-dielectric-constant media. Thus an important contribution from electrical interaction energies is expected even for associated solutes in these solutions. Unfortunately, no statistical-thermodynamic theory is available yet to estimate the non-ideality of such solutions. I believe that an important breakthrough to a rigorous theory for solvent extraction depends on the development of a treatment of this problem.

A solution of this problem is seen to be crucial for an understanding of non-specific interactions in organic solvents, *i.e.* those not expressible by means of the formation of new chemical species, governed by mass-action law equations. An outstanding problem of this kind is third-phase formation, *i.e.* the splitting of the organic phase into two mutually immiscible ones. This has been explained qualitatively in terms of the rearrangement of dipoles of the solute relative to their arrangement at lower concentrations. When these are arranged in an antiparallel array, they are relatively less polar and more compatible with the non-polar diluent, whereas when they rearrange to a parallel array, they are ejected. An attempt at a quantitative treatment of this situation has been made<sup>9</sup>, but we are still a long way from a comprehensive treatment with a minimum of free parameters. With some

extraction systems, namely those involving amphipatic extractants, the difficulties are increased by the phenomenon of micelle formation, in particular the formation of inverted micelles. The available theories of surfactant chemistry have not yet been applied to this case, and thereby to solvent extraction systems. This might be a big step forward for such systems of, say, long-chain ammonium salt or dinonylnaphthalene sulphonate extractants.

Let us now finally see how the above considerations of non-ideal behaviour enter into the apparent failure of the law of mass-action when applied, for example, in the slope analysis method<sup>10</sup>. Consider the following general extraction reaction:



where species in the organic phase are overlined, I is the distribuend and S the solvent, in an appropriate diluent. What we want to know is the composition (as a first step) of the species of I swimming around in the organic phase, that is the value of  $p$ . Let the equilibrium constant for this reaction be  $K$ , then

$$[\bar{I}S_p] = K[I]y_I [\bar{S}]^p \bar{y}_S^p \bar{y}_{IS_p}^{-1} \quad (4)$$

What we measure is  $D = \bar{C}_I/C_I$  as a function of  $\bar{C}_S$ , and what we are after is the value of  $p$ . Obviously the first step is to relate the total concentration of the participants in the extraction with those of the species. Here we are against a stoichiometric problem, rather than one of non-specific non-ideality. So we may introduce the explicit assumptions  $[\bar{I}S_p] = \bar{C}_I$  and  $[I] = C_I$ . These may be tested independently, and should not concern us if we accept them as valid. Then we may set  $[\bar{S}] = \bar{C}_S$ , making an additional, this time mathematical, assumption of neglecting  $p\bar{C}_I$  compared with  $\bar{C}_S$ . Sometimes people forget to see whether this is justified for their conditions. Suppose it is. We can now rearrange the above equilibrium expression into one relating  $D$  to  $\bar{C}_S$ , which becomes in logarithmic form:

$$\log D = \log K + p \log \bar{C}_S + \log y_I + p \log \bar{y}_S - \log \bar{y}_{IS_p} \quad (5)$$

Now we hopefully perform the partial differentiation

$$(\partial \log D / \partial \log \bar{C}_S)_{C_I, \bar{C}_I} = ? \quad (6)$$

We immediately see that this is impossible, since as  $D$  varies we cannot keep both  $C_I$  and  $\bar{C}_I$  constant, and these, in turn, affect the activity coefficients. Sometimes we succeed in circumventing this difficulty by providing a constant aqueous phase and such low concentrations of the distribuend that  $y_I$  is a constant, and  $\bar{y}_{IS_p}$  becomes independent of  $\bar{C}_I$ . One must be careful now, however, since addition of the electrolyte to the aqueous phase may cause the assumption  $[S] = \bar{C}_S$  to become invalid. The electrolyte often being well extractable, binds some of the extractant, and since it is present at macro concentrations, may bind an appreciable fraction of it. Suppose that we succeed in selecting a non-extractable electrolyte. There is one other implicit assumption which most of us overlook in trying to make the desired partial differentiation. This is that the activity of the water remains constant.

This is necessary for  $y_I$  remaining constant as  $\bar{C}_S$  varies, since coupling interactions involving I and water and S and water make  $y_I$  depend on  $\bar{C}_S$ .

We may now perform the partial differentiation, taking care to keep not the initial concentrations of electrolyte, distribuend, etc. and the activity of water constant, but their equilibrium values. This may necessitate a series of experimental runs at different initial concentrations, and appropriate interpolations. Experiments are indeed rarely done according to this requirement. Suppose they have, and then:

$$(\partial \log D / \partial \log \bar{C}_S)_{c_1, c_{\text{electrolyte}}, a_{\text{H}_2\text{O}} \dots} = p + p(\partial \log \bar{y}_S / \partial \log \bar{C}_S) - (\partial \log \bar{y}_{IS_p} / \partial \log \bar{C}_S) \quad (7)$$

One final assumption is implicit here, namely that the index  $p$  is independent of  $\bar{C}_S$

We have considered a very simple distribution equilibrium, with simple stoichiometry and only three species involved, and have designed our experiments with the utmost caution, to avoid all complications. At this stage, however, we can no longer ignore the non-specific non-idealities in the organic phase. In order for S to be an extractant it must be sufficiently polar to interact with I, and even the solvated species  $IS_p$  may be polar. Thus neither  $\log \bar{y}_S$  nor  $\log \bar{y}_{IS_p}$  should be taken as equalling zero. Nor should they be taken as constants, independent of  $\bar{C}_S$ , as has been discussed above. The theories available for organic solutions, such as the regular solution-solubility parameter approach, are not valid for polar solutes, and there is very little guidance for estimating these activity coefficients. It has been claimed that, although the activity coefficients for S and  $IS_p$  may vary individually, their ratio  $\bar{y}_{IS_p} / \bar{y}_S$  may be independent of  $\bar{C}_S$ . In view of the large discrepancy in their size this is unlikely. An empirical relationship  $\log \bar{y}_S = k_S \bar{C}_S$  has been found for some solutions of polar solutes in organic diluents.<sup>11</sup> Even if true for the binary solutions, this may not hold for the wet solutions obtained on extraction.

For lack of any better solution to this problem, let us accept these two approximations, ending up with the simple expression

$$(\partial \log D / \partial \log C_S)_{c_1, c_{\text{electrolyte}}, a_{\text{H}_2\text{O}}} \simeq p + (p - 1)k_S \bar{C}_S \quad (8)$$

We should perhaps not try to extrapolate the left hand side of this equation to  $\bar{C}_S = 0$ , because of the possible nonconstancy of the solvation number  $p$  as the extractant is further and further diluted. We may, hopefully, obtain a meaningful value of  $p$ , and thus an indication of the composition of the species swimming around in the solution, by obtaining  $k_S$  independently, and correcting for the second term on the right hand side by iterations. Thus, after a lot of labour, we have solved our problem.

Now, is it not extremely vexing that we find empirically from the simplest experimental data that:

$$d \log D / d \log C_S = \text{constant}$$

and that this constant equals a stoichiometric index  $p$  which is integral within an uncertainty of say  $\pm 0.05$  units, shows no trend with  $\bar{C}_S$  whatsoever, and is chemically reasonable? Yes, indeed, and we should worry if this

happens to us too often, since the fortuitous cancellation of the nonspecific nonideality effects might be due to some personal bias, and preference for beautiful straight lines.

In conclusion, therefore, we see that slope analysis is indeed a wonderfully simple method for studying distribution equilibria. "Wonderfully", because it works nicely rather too often, even in complicated equilibria, with known side reactions with ligands and hydrogen ions of both distribuend and extractant, on top of any self-aggregation effect they might show. Of course, slope analysis is just one way of applying the law of mass-action to distribution equilibria, and the availability of high speed digital computers encourages people to apply it to more and more complicated systems, sometimes with complete disregard of those interactions, which cannot be stated in terms of formation of chemical species.

## References

- <sup>1</sup> L. G. Sillén. in *Solvent Extraction Chemistry*, (Eds. D. Dyrssen, J. O. Liljenzin and J. Rydberg), North Holland Publ. Co., Amstrdam, 1967.
- <sup>2</sup> D. F. Peppard, G. W. Mason and G. Griffin. *J. Inorg. Nucl. Chem.*, **27**, 1683 (1965); J. F. Ferraro, G. W. Mason and D. G. Peppard, *ibid.*, **22**, 285 (1961); C. F. Baes. *J. Phys. Chem.* **66**, 1629 (1962); *J. Inorg. Nucl. Chem.*, **24**, 707 (1962); J. R. Ferraro and D. F. Peppard. *J. Phys. Chem.*, **67**, 2639 (1963).
- <sup>3</sup> G. R. Choppin and P. J. Unrein. *J. Inorg. Nucl. Chem.*, **25**, 387 (1963); N. C. Li and coworkers, *ibid.*, **14**, 255 (1960); **16**, 337 (1961); **27**, 2093 (1965); T. Ishimori and coworkers. *Nippon Genshuryoku Gakkaishi*, **3**, 193, 590, 684 (1961).
- <sup>4</sup> D. E. Metzler and R. J. Myers. *J. Am. Chem. Soc.* **72**, 3776 (1950).
- <sup>5</sup> W. Davies, Jr. *Nucl. Sci. Eng.* **14**, 159, 169, 174 (1962); C. J. Hardy, D. Fairhurst, H. A. C. McKay and A. M. Willson. *Trans. Faraday Soc.*, **60**, 1262 (1964).
- <sup>6</sup> V. V. Fomin and V. T. Potapova. *Zh. Neorg. Khim.*, **8**, 990 (1963); W. Müller and R. M. Diamond. *J. Phys. Chem.*, **70**, 3469 (1966).
- <sup>7</sup> G. Markovits and A. S. Kertes, in *Solvent Extraction Chemistry*, North Holland Publ. Co., Amsterdam, p. 390 (1967); E. Högeföldt and coworkers. *Trans. Roy. Inst. Techn. Stockholm*, Nos. 226-229 (1964).
- <sup>8</sup> Y. Marcus and A. S. Kertes. *Ion Exchange and Solvent Extraction of Metal Complexes*, Wiley-Interscience, London, 1969, p. 441; V. B. Shevchenko and coworkers. *Radiokhimiya*, **1**, 257 (1959).
- <sup>9</sup> H. L. Friedman. *J. Phys. Chem.* **66**, 1595 (1962).
- <sup>10</sup> Reference <sup>8</sup>, pp. 461-467.
- <sup>11</sup> E. Hesford and H. A. C. McKay. *Trans. Faraday Soc.*, **54**, 573 (1958).