

# The 'salting out' effect: investigating the influence of both the nature and concentration of salt on the partition coefficient of butan-1,4-dioic acid

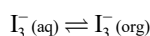
John McCullagh

**ABSTRACT** This sixth-form chemistry activity describes how students can use acid–base titrimetry to investigate how adding salt to the aqueous phase may change the value of the partition coefficient of an organic acid between water and 2-methylpropan-1-ol. While the presence of lithium chloride and sodium chloride increases the value of the partition coefficient (the acid favouring the organic to the aqueous phase), the chlorides of potassium and caesium have the opposite effect. The activity provides a practical context for a full investigation and a discussion of the general principles of polarity, intermolecular forces and solubility.

The partition of a solute between an aqueous and non-aqueous phase relates to several areas of the school chemistry curriculum and, as a concept, relates to molecular structure, solubility and equilibrium. The addition of an electrolyte to the aqueous phase during solvent extraction is a well-established method for ensuring that the maximum amount of solute passes from the aqueous into the organic phase. This principle, known as 'salting out', is defined as *'the addition of particular electrolytes to an aqueous phase in order to increase the distribution ratio of a particular solute'* (Incedy, Lengyel and Ure, 1998). Although calculating the distribution coefficient of a solute between two phases is no longer a requirement, the popular A2 specifications (AQA, 2015: 58; Edexcel, 2015: 40; Council for the Curriculum, Examinations and Assessment, 2016: 40) include the synthesis of phenylamine by the reduction of nitrobenzene, followed by extraction into ether. The addition of sodium chloride to the aqueous phase maximises the yield of phenylamine (Vogel, 1978). At AS-level, students are required to understand that *'extraction with a solvent in a separating funnel'* (Edexcel, 2016: 20) is included as a technique used in the preparation and purification of compounds. It is also exploited during the preparation of soap following the reaction of concentrated sodium hydroxide with

an oil or fat. The concept of 'salting out' is also important in analytical chemistry where low levels of pesticides and herbicides are transferred from a large volume of water samples into an organic phase before analysis by gas–liquid chromatography. The addition of a small amount of simple salts increases the efficiency of this extraction.

The topic of partition provides an example of a homogeneous equilibrium, such as the partition (equation shown below) of the triiodide ion between water and non-aqueous solvents, and can support discussions of the relationship between molecular structure and the concepts of polarity and solubility.



The investigation requires students to plan, carry out and evaluate their data in a systematic way. The practical work could either be carried out over a period of time by an individual student or adapted for a whole class, where students each carry out a specific part. An investigation into the relationship between the length of the hydrocarbon chain of dicarboxylic acids and their partition between water and 2-methylpropan-1-ol has been reported (McCullagh, 2004). By titrating samples of each phase against NaOH solution, students can calculate the concentration of organic acid in each phase and hence the value of the partition

coefficient. The values for the series of dicarboxylic acids from ethanedioic (oxalic acid,  $n=2$ ) through to heptanedioic acid (pimelic acid,  $n=7$ ) can be determined and plotted. This investigation provides students with the opportunity to explore the concepts of intermolecular forces, polarity and solvation through fairly straightforward practical work. It challenges students to consider the molecular structure of solutes and how the presence of hydrophobic and hydrophilic segments of the molecule may influence solubility.

Having looked at how the nature of the solute influences the partition coefficient, it might be interesting to allow students to consider the nature of the solvent and explore how the polarity of each of the phases may influence partition. A convenient and simple way to alter the nature of the aqueous phase is simply to add salt. The following investigation challenges students to consider:

- How does the amount of a salt influence the value of the partition coefficient?
- How does the nature of the metal cation influence the value of the partition coefficient?

### Health and safety

Safety goggles and protective gloves must be worn throughout and the activity must be carried out in a well-ventilated laboratory.

- **2-methylpropan-1-ol:** This is classified by CLEAPSS (2016) as flammable liquid and vapour, causes skin irritation, causes serious eye damage, may cause respiratory irritation, may cause drowsiness or dizziness. The practical should be carried out away from naked flames and in a well-ventilated space. The compound should be handled with care using protective gloves. Direct pipetting from the bottle will reduce exposure.
- **NaOH (0.1 mol dm<sup>-3</sup>):** As the concentration is less than 0.5 mol dm<sup>-3</sup> but more than 0.05 mol dm<sup>-3</sup>, CLEAPSS (2016) classifies this as 'irritating to the skin and eyes'.
- **Butan-1,4-dioic acid:** CLEAPSS (2016) – moderately toxic by ingestion, and an eye irritant. Wear protective gloves and eye protection when handling.
- **Phenolphthalein solution:** Highly flammable.
- **LiCl:** Harmful if swallowed. Irritating to eyes and skin.
- **NaCl:** Ingestion in large quantities can cause poisoning.

- **KCl:** Ingestion can cause poisoning.
- **CsCl:** Moderately toxic by ingestion (CLEAPSS, 2016).

### Method

- 1 Aqueous solutions of LiCl, NaCl, KCl and CsCl were prepared with concentrations in the range 0.20–5.00 mol dm<sup>-3</sup>, as shown in Table 1. Stock solutions of the highest concentration of each salt were prepared and then diluted for each range of solutions.
- 2 Butan-1,4-dioic acid (0.59 g, 0.10 mol dm<sup>-3</sup>) was dissolved in 50 cm<sup>3</sup> of each salt solution and shaken with 50 cm<sup>3</sup> of 2-methylpropan-1-ol for 3 minutes in a stoppered reagent bottle.
- 3 After standing for 5 minutes, each layer was sampled as follows. A 10.0 cm<sup>3</sup> aliquot of the top organic phase was sampled in duplicate using a pipette and pipette filler and transferred to a conical flask. A 10.0 cm<sup>3</sup> portion of distilled water was added (using a measuring cylinder) to the same conical flask.
- 4 In the same way, a 10.0 cm<sup>3</sup> portion of the aqueous (lower) phase was sampled. Contamination from the top phase can be minimised by, before fitting the pipette filler, placing your index finger over the end of the pipette while it passes through the upper organic phase. Then fit the pipette filler and sample as before. The aqueous phase was also sampled in duplicate.
- 5 The concentration of butan-1,4-dioic acid was then determined by titration with NaOH (0.10 mol dm<sup>-3</sup>) using phenolphthalein as indicator. Rinsing down of the side of the flask with distilled water during titration of the organic phase is recommended. With care, titres can easily be obtained to within 0.05 cm<sup>3</sup>. The mean value of two titrations was taken for each phase and was then used to calculate the concentration of the organic acid in each phase and hence the partition coefficient. The titration flask should be shaken continuously during the addition of the NaOH to the organic layer to ensure that all the acid in the organic layer has reacted.

The method above was also used to determine the partition coefficient of butan-1,4-dioic acid between 2-methylpropan-1-ol and distilled water. An additional useful exercise is to require students to use the titre values for both phases to demonstrate that the total mass of butan-1,4-dioic

acid used in the experiment has been accounted for across both phases.

## Results

Sample data for  $5.0 \text{ mol dm}^{-3}$  LiCl are given here:

- Mean titre for organic phase =  $13.13 \text{ cm}^3$ .
- Mean titre for aqueous phase =  $5.58 \text{ cm}^3$ .

### Organic phase:

- $13.13 \text{ cm}^3$  of  $0.1 \text{ mol dm}^{-3}$  NaOH contains  $1.313 \times 10^{-3}$  moles of NaOH.
- As each mole of acid requires two moles of alkali, this is equivalent to  $6.57 \times 10^{-4}$  moles of butan-1,4-dioic acid in  $10 \text{ cm}^3$  of the organic phase.
- The concentration of butan-1,4-dioic acid in the organic phase is thus  $(1000/10) \times 6.57 \times 10^{-4} = 0.0657 \text{ mol dm}^{-3}$ .

### Likewise for the aqueous phase:

- The concentration of butan-1,4-dioic acid in the aqueous phase is  $0.0279 \text{ mol dm}^{-3}$ .

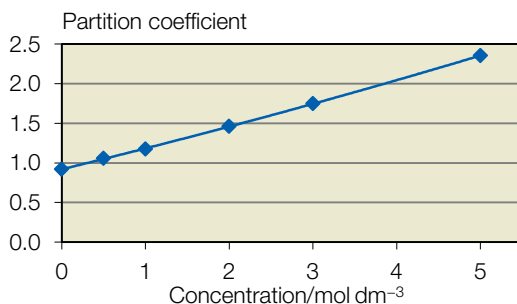
$$K_d = \frac{[\text{butan-1,4-dioic acid}]_{(\text{org})}}{[\text{butan-1,4-dioic acid}]_{(\text{aq})}} = 2.35$$

The titres were recorded and partition coefficients calculated over the range of concentrations for each of the salts, as shown in Table 1.

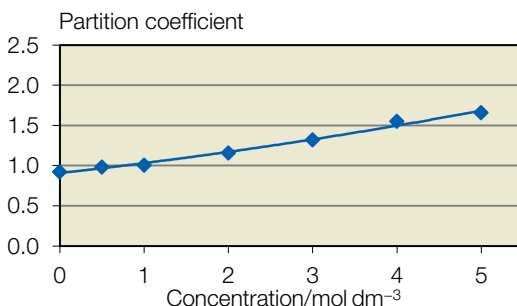
**Table 1** The variation in partition coefficient with concentration for each of the salts LiCl, NaCl, KCl and CsCl

Salt concentration ( $\text{mol dm}^{-3}$ )	Partition coefficient			
	LiCl	NaCl	KCl	CsCl
0	0.92	0.92	0.93	0.92
0.20	–	–	0.92	0.91
0.50	1.06	0.98	0.89	0.87
1.00	1.17	1.01	0.89	0.80
2.00	1.46	1.15	0.88	0.72
3.00	1.75	1.32	0.85	–
5.00	2.35	1.66	–	0.53

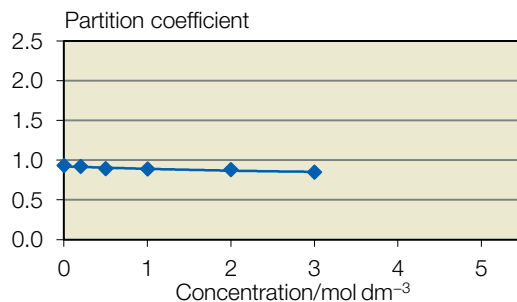
The values of partition coefficient versus concentration of salt are plotted for LiCl (Figure 1), NaCl (Figure 2), KCl (Figure 3) and CsCl (Figure 4). Figure 5 shows a plot of the partition coefficient for a  $1.0 \text{ mol dm}^{-3}$  solution of each metal salt, and for distilled water for comparison.



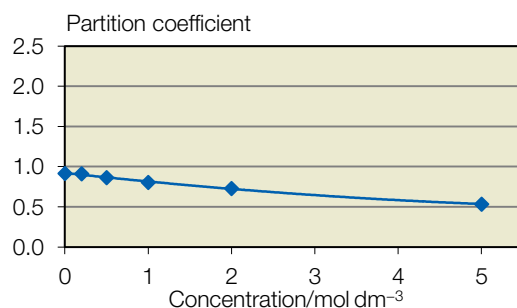
**Figure 1** The variation in partition coefficient of butan-1,4-dioic acid with concentration of LiCl



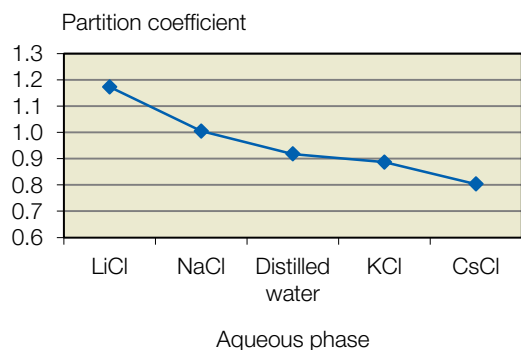
**Figure 2** The variation in partition coefficient of butan-1,4-dioic acid with concentration of NaCl



**Figure 3** The variation in partition coefficient of butan-1,4-dioic acid with concentration of KCl



**Figure 4** The variation in partition coefficient of butan-1,4-dioic acid with concentration of CsCl



**Figure 5** The variation in partition coefficient with the nature of the aqueous phase; all salt concentrations are  $1.0 \text{ mol dm}^{-3}$

## Discussion

The results show that the presence of salt changes the value of the partition coefficient and that the size of this change increases with the concentration of salt. What is initially surprising is that, while LiCl and NaCl both produce the anticipated salting out effect (an increase in the value of the partition coefficient), the reverse effect is observed for solutions of KCl and CsCl.

The increase in the value of the partition coefficient brought about by the presence of LiCl and NaCl can be considered to result from the increase in the polarity or ionic nature of the aqueous phase decreasing the solubility of the butan-1,4-dioic acid. As the concentration of both salts increases, the solubility of the acid in the aqueous phase decreases, and so the partition coefficient increases. This result is consistent with the general principle of salting out and is exploited when we wish to ensure the maximum amount of organic material is extracted into a non-aqueous phase. It is of interest that LiCl has a greater effect on the partition coefficient than NaCl. Perhaps this is a result of its smaller size and therefore its greater 'charge density' or polarising effect on the aqueous phase.

The decrease in the partition coefficient brought about by the addition of potassium and caesium salts may surprise the students and therefore prompt them to think more deeply in search of an explanation. In these cases, butan-1,4-dioic acid is less soluble in the organic phase. This effect could therefore be considered as a 'salting in' effect. The reason may be that both KCl and CsCl are themselves quite soluble in

2-methylpropan-1-ol. Students will already be familiar with the use of potassium salts in organic reactions. Solubility data (Merck, 2001; Perry and Phillips, 1995) for these metal chlorides in ethanol reports sodium as 'very slightly soluble' and lithium, potassium and caesium as 'soluble'. During the shaking of the two phases, the salts may themselves dissolve in the organic phase, increasing its polarity and thereby decreasing the solubility of the butan-1,4-dioic acid molecules. The presence of salt in the organic phase could also be considered to result in less room for the butan-1,4-dioic acid and therefore decrease its solubility.

This investigation requires students to plan, carry out and report on a systematic study of a simple equilibrium system of both practical and theoretical importance. The AQA (2015: 77–78) specification requires students to 'identify variables including those that can be controlled', and encourages teachers to 'vary their approach to these practical activities. Some ... allow opportunities for students to develop investigative approaches.' The Edexcel (2015: 5) specification states that pupils 'should be able to design and carry out both the core practical activities and their own investigations, collecting data which can be analysed and used to draw valid conclusions.' In providing students with the opportunity to consider the nature and quantity of salt required to bring about a salting out effect, the investigation also provides a scenario for pupils to 'explain why chemists ... design production methods ... that have a high percentage atom economy' (AQA, 2015: 63). When planning, the students will have to decide on the volumes and concentrations of the reagents required. The measurement of often only small changes in titre values and thus partition coefficients requires both precision and accuracy. The data will provide opportunities for developing numeracy skills and identifying trends and patterns in data.

Recent changes to the popular examination boards' specifications require teachers to base their practical work around a number of specific chemistry experiments and so no doubt restrict the opportunities for teachers to include other examples of practical chemistry. It is hoped, however, that this full investigation, or indeed aspects of it, may prove useful for chemistry clubs or research projects, if not within teaching specifications.

From making density towers and playing with 'lava lamps' in primary school (Royal Society of Chemistry, 2017) to separating organic liquids from water at key stages 3 and 4, the immiscibility of polar and non-polar liquids provides a range of fascinating learning activities for chemistry

students of all ages. This activity enables sixth-form students to continue to explore and 'play' with this phenomenon and to deepen their understanding of concepts such as polarity and solubility. As well as developing their practical and investigative skills, it may also increase their interest in chemistry.

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# Contribute to a proposed SSR 'special issue' on everyday science

Many students leave school thinking that science only happens in the science lab. This proposed theme will celebrate the science we derive from everyday objects, happenings and issues. It will stress the importance of teaching science as a unified set of ideas and methods, with topics such as:

- **photosynthesis** – which should be approached from its vital role in supplying life (biology) with materials (chemistry) and energy (physics);
- **leaves falling in autumn** – from the biology of trees, the physics of falling and air resistance and of colour and the associated biochemistry;
- **climate change** – from the chemistry of burning fossil fuels, the physics of the greenhouse effect, the geography/geology of the Earth and the biology of the carbon cycle;
- **cooking potatoes** – from the physics of heat and temperature, of boiling and evaporation, the chemistry of rates of reaction and the biology of food;
- **plastic recycling** – from the biology of ecosystems and biodegradation, the chemistry of oil and polymers and the physics of sunlight and colour;
- **drawing with a pencil** – from the biology of paper-making, the chemistry of carbon and the physics of light and sight.

And so the list can go on.

Suggested areas could be:

- the Salters' approach, and any other established schemes that are based on real-life issues and materials;
- other smaller scale ways in which science teachers are trying to teach in an integrated way using the everyday experiences of their pupils, especially where these have been successfully integrated into the constraints of examination straitjackets;
- experiences from primary science where this approach is pretty much established and where we are free of examinations.

But YOUR ideas count. How is the science we teach in school used in their lives outside school? How can examples from other experiences help inform our science teaching?

Anyone interested in contributing, either a full-length article or a short 'Science note', please get in touch.

As a first step, a quick note to suggest what you could contribute is all that it needs.

Please contact me by email – [keithaross@gmail.com](mailto:keithaross@gmail.com) – and please spread the word.

**Keith Ross**