Nonideal Behaviour of Binary Solvent Systems & Rf Values of Solutes in Paper Chromatography

T S RAO*  
Department of Chemistry, University of Poona, Pune 411007  
and  
S J BHASE  
Explosives Research and Development Laboratory, Pashan, Pune 411 021  

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Rf values in paper chromatography and solubilities of benzoic acid, phenylacetic acid and o-chlorobenzoic acid using the binary solvent systems, (i) toluene-benzene (ideal), (ii) cyclohexane-nitrobenzene (non-ideal, positive deviation) and (iii) chloroform-diisopropyl ether (non-ideal, negative deviation) have been obtained and the results discussed.

A mixture of solvents is often more effective than a single solvent for the separation of solutes in paper chromatography. However, it is likely that on varying the composition of a binary solvent system, the Rf value for a solute might also vary depending on the composition and the ideal/non-ideal behaviour of the system. Little information is available on the influence of the ideal/non-ideal behaviour of the binary solvent systems on Rf values. Hence the present work has been carried out to investigate this aspect.

The following binary solvent systems were studied: (i) toluene-benzene (ideal), (ii) cyclohexane-nitrobenzene (non-ideal, positive deviation) and (iii) chloroform-diisopropyl ether (non-ideal, negative deviation). The solvents constituting these systems were BDH products and were distilled before use. The solutes employed were: benzoic acid, phenylacetic acid and o-chlorobenzoic acid (all BDH reagents). Whatman No. 1 filter paper was used as the stationary phase.

For each solvent system six mixtures were prepared in which the mole fraction of the first component was 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 respectively. The chromatograms were run at 25°C ± 0.1°C on four paper strips (15 cm × 5 cm) for each solvent composition and the position of the solute was located by spraying 0.05% bromocresol green solution over the strips. In order to ensure the accuracy of Rf values, the preparation of all the strips and their development were carried out simultaneously under identical experimental conditions. The Rf values were reproducible within ±0.01 for any composition of the solvent.

The solubility of each solute in each solvent system was determined by saturating the system with the solute at 25°C and determining the concentration by titration with standard barium hydroxide solution using a baryta burette.

It is observed that the Rf value-composition curve for the ideal solvent system (i) is linear. For the systems (ii) and (iii) the curves show negative and positive deviations from linearity respectively. A comparison with the total vapour pressure-composition curve (ideal/non-ideal behaviour) shows an inverse relation between the two curves for the solvent systems (ii) and (iii).

The Rf value of the solutes have been reported to be directly related to solubilities in the mobile phase. It is observed that the solubility-composition curves for the system (i) is similar to the Rf value-composition curve. For the systems (ii) and (iii) the solubility-composition curves show positive and negative deviations from linearity, respectively. Hence it is expected that the Rf value-composition curves should also evince similar variations. However, contrary to expectation, an inverse relation between Rf value and solubility is observed in these cases.

In the non-ideal systems it is likely that the polar stationary phase on the filter paper imbibes the more polar component (nitrobenzene/diisopropyl ether) of the binary solvent system in preference to the less polar component (cyclohexane/chloroform). Now the solute is more soluble in nitrobenzene/chloroform than in cyclohexane/diisopropyl ether. Hence the solute is present in the stationary phase in system (ii) to a greater extent while in system (iii) to a less extent than expected from ideal behaviour. This results in a lower Rf value in system (ii) and a higher Rf value in system (iii) than in ideal system. Thus the observed inverse relation between Rf value and ideal/non-ideal behaviour of the binary solvent system arises out of the preferential enrichment of the more polar component from the binary system.

References

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