SOLVENT PROBLEMS IN INDUSTRY

Edited by

GEORGE KAKABADSE

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PREFACE

This book places emphasis on solvent problems in industry and aims to rationalise the relationship between solvent properties and economic use of solvents. It is largely a report of the proceedings of the 'European (4th UMIST) Solvents Symposium for Industry', jointly organised by industry and UMIST in 1983. The scope of this volume has been enlarged by including some material presented at the 3rd Solvents Symposium for Industry in 1980 and duly updated in 1983. The excellent attendance at the four solvents symposia for industry (1974–83), the first of their kind, is a clear indication of a need for presenting and discussing solvent problems in industry and for highlighting new developments. In this book, solvent topics are viewed under four sections, viz. 'General', dealing with fundamental and broader aspects of solvents; 'Applied', listing selected solvent applications; 'Solvent Recovery and Disposal', stressing the economic and environmental issues involved; and finally, the ever changing aspects concerning 'Health, Legislation and Safety', including the latest EEC directives for labelling of solvents.

The text is intended mainly for industrial personnel dealing with solvents but it may also prove useful to chemists, chemical engineers and management scientists at universities and polytechnics interested in solvents, which have a vast market.

I am greatly indebted to my industrial co-organisers and their respective companies without whose cooperation and assistance the solvents symposia would not have been possible: Charles Andrews (Solvents Consultant), Brian Atkinson (Petrofina UK), Giuliano Ballini (Montedipe), Brian Davis (Hoechst UK), Barry Hudson (BP Chemicals), John Revell (Ford Motor Company), Mike Smith (Esso Chemicals), Richard Williams (Shell Chemicals), Ken Wright (ICI plc, Organics Division). I should also like to express my thanks to my wife for proof-reading and constant encouragement and to the following colleagues at UMIST: John Belcher, Alan Beresford, Jenny Curtis, Roger Perry, Bob Ramage, Neville Smith and Tony Tipping.

Particular thanks are given to my co-authors, recognised experts in their own field, who willingly interrupted their busy routine to present an up-to-date account of their invited papers.

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PART I

GENERAL ASPECTS

1

WHAT ARE SOLVENTS?

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ABSTRACT

In an ideal solution, each solute molecule is independent of all other solute molecules. Thus solvents keep solute molecules apart. A related task for solvents is to disperse pure substances (solid or liquid) into solution. Both dispersal and separation require some stabilisation of solutes in solution through solvent–solute interactions. Solvents can also support otherwise transient species, e.g. the proton as H_3O^+ and the electron as the 'solvated electron'. In other systems, solvents play a key rôle in determining the conformation of solutes.

The position of a chemical equilibrium can be altered by appropriate choice of solvent (and the temperature of the solvent). New solute species, such as ion-pairs, can be formed in solution by choosing a solvent having low permittivity. A similar rôle is played by solvents in controlling the rate of chemical reaction. Some solvents are also chosen because they provide a medium for catalytic reactions.

1. INTRODUCTION

As a matter of definition, a solution comprises at least two components.[1] The component which is in large molar excess, and normally a liquid in the pure state at the same temperature and pressure as the solution, is called the *solvent*. The minor component is called the *solute*. Somewhat perversely, when discussing the properties of solutions our main concern is with the properties of solutes. Often a particular solvent is chosen because there is a particular property of a

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solute which we wish to either develop or exploit. Therefore in attempting to answer the question posed by the title to this article, we consider how solvents influence the properties of solutes. This is an enormous subject. Here we use thermodynamics as the basis for our discussion.

2. CHEMICAL POTENTIALS

We confine attention to systems held at constant temperature and constant pressure. The dependent extensive variable called the Gibbs function can be defined by the set of independent variables T, p and n_i, where n_i represents the number of moles of independently defined chemical substances in the system n_1, n_2, n_3. . . . , n_i. The chemical potential μ_j of a given substance j (i.e. one of the set of i-substances) is defined by the following partial derivative:

$$\mu_j = (\partial G/\partial n_j)_{T,p,n_{\neq i}} \tag{1}$$

If substance j is a solute in solution, the chemical potential of j is related, by definition,[2] to the molality m_j by the equation:

$$\mu_j(\text{sln}; T; p) = \mu_j^{\ominus}(\text{sln}; T) + RT \ln (m_j \gamma_j / m^{\ominus}) + \int_{p^{\ominus}}^{p} V_j^{\infty}(\text{sln}; T; p)\, dp \tag{2}$$

Here $\mu_j^{\ominus}(\text{sln}; T)$ is the chemical potential of j in its solution standard state where $m_j = 1$, $\gamma_j = 1$ at temperature T and standard pressure $p^{\ominus}$. The quantity $V_j^{\infty}(\text{sln}; T; p)$ is the partial molar volume of j in solution at infinite dilution. The activity coefficient γ_j is defined using:

$$\text{Lt} (m_j \to 0) \gamma_j = 1 \cdot 0 \tag{3}$$

at all T and p. Thus in an ideal solution $\gamma_j = 1 \cdot 0$; each solute molecule behaves independently of all other solute molecules in solution. In these terms, the basic rôle of a solvent is to keep solute molecules apart and thereby to insulate them from each other. In real solutions, solute–solute interactions account for deviations from ideal. Indeed these deviations can be quite marked where solute–solute interactions are strong and long-range, e.g. between ions in a salt solution.[3]

We have turned the question concerning solvents into a discussion of the properties of solutes. However the terms, solute and solvent, are simply convenient labels attached to different components of the same

system. Indeed the properties of all components in a system are linked through the Gibbs–Duhem equation:

$$S\, dT - V\, dp + \sum_{j=1}^{i=i} n_j\, d\mu_j = 0 \tag{4}$$

For solutions, eqn (4) describes a communication between solutes and solvent.

3. STANDARD CHEMICAL POTENTIALS

The standard chemical potential $\mu_j^{\ominus}(\text{sln}; T)$ of solute j in solution is the parent of a family of standard partial molar properties including the standard enthalpy $H_j^{\ominus}$, standard volume $V_j^{\ominus}$, standard entropy $S_j^{\ominus}$ and standard heat capacity at constant pressure $Cp_j^{\ominus}$. These quantities are related through well-known thermodynamic equations; e.g. the Gibbs–Helmholtz equation:

$$[\partial(\mu_i^{\ominus}/T)/\partial T] = -H_i^{\ominus}/T^2 \tag{5}$$

Nevertheless we cannot calculate an absolute value for $\mu_j^{\ominus}(\text{sln}; T)$. All that we can do is to discuss differences between the chemical potentials of j in different standard states. Thus with reference to two phases, α and β, we can consider the quantity $\Delta(\alpha\rightarrow\beta)\mu_j^{\ominus}(T)$ and related parameters such as $\Delta(\alpha\rightarrow\beta)H_j^{\ominus}(T)$. These Δ-quantities can be thought of as describing the *transfer* of j from α to β. Here we meet another rôle played by solvents, namely *dispersal*. If, for example, α is the pure component j (solid or liquid) and β is a solvent, the quantity $\Delta(\alpha\rightarrow\beta)\mu_j^{\ominus}(T)$ refers to the dispersal of pure j into solution. This transfer is characterised experimentally by the solubility. The processes of dispersal and separation rely on the stabilising influence of solute–solvent interactions.

4. SOLUTE–SOLVENT INTERACTIONS

An alternative heading to this section would be 'Intermolecular Forces' because we are concerned with the interaction between solute j and neighbouring solvent molecules and, as important, the interactions between solvent molecules which surround solute j. A useful approach in this context was suggested by Gurney.[4] A solute in solution is

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surrounded by a co-sphere of solvent within which the organisation of solvent differs from that of the bulk solvent outside the co-sphere. Hence solute–solvent interactions are described in terms of solute–co-sphere solvent interactions. The range of these interactions is briefly commented on in this section.

The important rôle played by van der Waal forces in solute–solvent interactions is borne out by solubility data[5] for non-electrolytes in liquids. These data can be considered from two standpoints[6,7] (Fig. 1). The solubilities of a given solute in a range of solvents are related to the Hildebrand solubility parameter δ_1 $[=(\Delta_v E_1^{\ominus}/V_1^*)^{1/2}$ where $1 =$ solvent]. Thus δ_1 is a measure of the strength of intermolecular forces within a solvent. Alternatively the solubilities in a given solvent of a number of solutes are related to the Lennard–Jones force constant for gaseous solutes, ε. The latter quantity provides a measure of the repulsion–dispersion forces involving the solute.
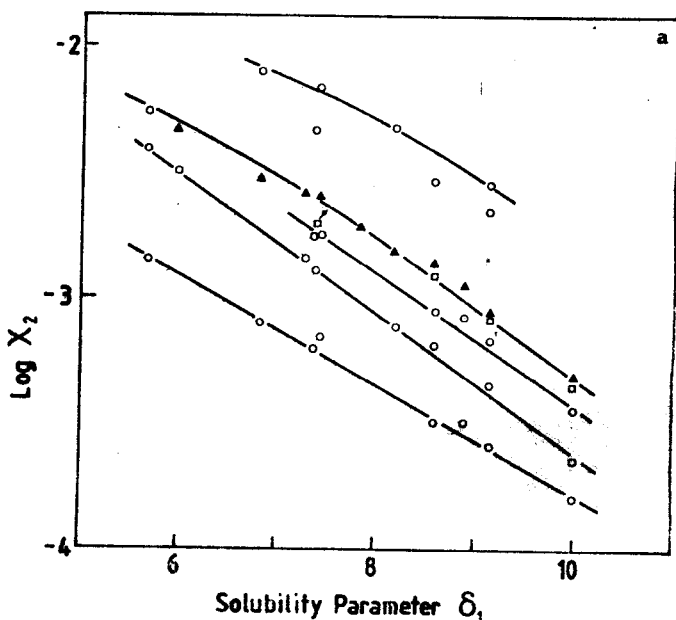

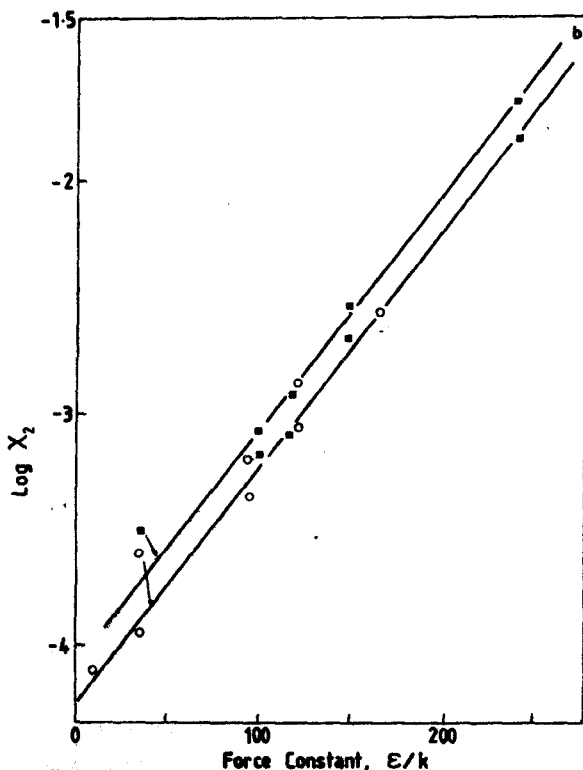Fig. 1. Solubilities of apolar solutes: (a) dependence of solubility on Hildebrand parameter δ_1 for solvent.

Fig. 1—contd. (b) Dependence of solubility in a given solvent on Lennard-- Jones force constant for solute (re-drawn from Ref. 7).

The subtlety of solute–solvent interactions is borne out by the dependence of solubility of apolar solutes on the composition of a liquid mixture. In the example[8] given in Fig. 2, we see how the solubility can be controlled by modest changes in the composition of the solvent, although the underlying relationship between solubility and composition is complicated.

With increase in intensity of solute–solvent interactions, so the possibility emerges of a specific interaction between solute j and a single neighbouring solvent molecule. The high solubility of iodine in
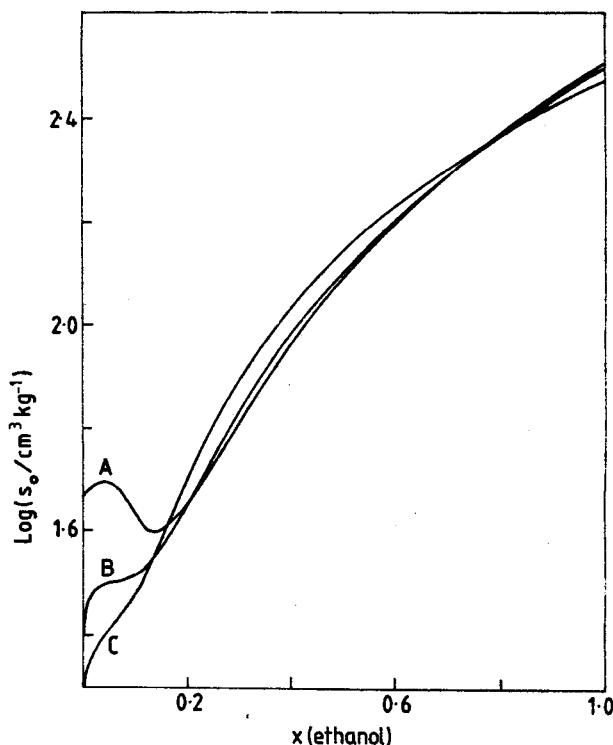
Fig. 2. Solubility of argon in ethanol + water mixtures as a function of mole fraction of alcohol, x_2; (a) 227·2 K, (b) 303·0 K and (c) 333·3 K (re-drawn from Ref. 8).

benzene and the intense colour of many otherwise simple solutions provides the starting point for examination of charge–transfer complexes and donor–acceptor complexes.[9]

A particularly important interaction between solute and solvent is hydrogen bonding.[10] Spectroscopic evidence for this interaction is compelling. For example,[11] very dilute solutions of CH_3OH in tetrachloromethane show an absorbance band in the $3600 \, cm^{-1}$ region which is assigned to the O—H stretching vibration of CH_3OH (Fig. 3). When CH_3I is added to the solution, the intensity of this band