

XIIth
International
Conference
in
Organic Coatings
Science
and
Technology

Proceedings 12

7-11 July 1986
Athens, Greece

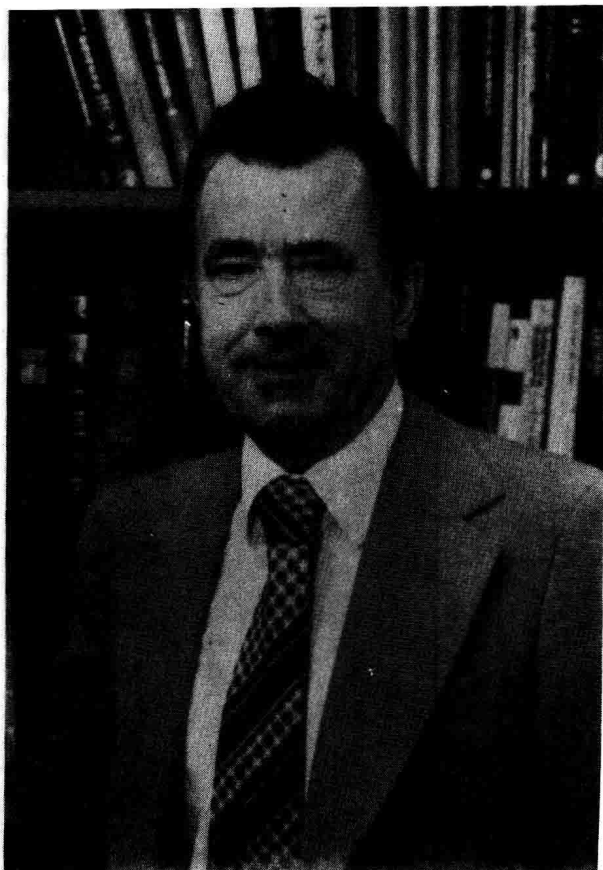
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IN MEMORIAM



Geoffrey D. Parfitt

TWELFTH INTERNATIONAL CONFERENCE
IN
ORGANIC COATINGS SCIENCE AND TECHNOLOGY

ATHENS, GREECE

7 - 11, JULY, 1986

P R E F A C E

The purpose of the conference is to bring together leading scientists, engineers, industrialists, and educators in an international forum to discuss all aspects of organic coatings science and technology, including inks. The sponsors hope that such an interchange of ideas and information will enable the industry to establish more productive programs of research, development and production, as well as to increase the rate of useful technological innovations.

The conference has been designed for chemists or other professionals who want to understand the principles involved in the science and technology of organic coatings - their manufacture, applications to surfaces, and properties. In addition, the latest developments in the field of organic coatings will be presented in a manner which will permit the scientist or engineer to integrate fundamental scientific principles with processing and application technology.

This conference is endorsed by the Polymeric Materials: Science and Engineering Division of the American Chemical Society and co-sponsored by the Greek Society of Paints Industries.

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PHASE EQUILIBRIA IN COATINGS

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ABSTRACT

This article is concerned with bulk phase equilibria in coatings. A number of technological problems relating to the subject are discussed followed by a brief survey of the different types of models on polymer solution thermodynamics. Different methods for predicting phase equilibrium phenomena are evaluated with the emphasis on solubility parameter and group contribution approaches. A new group contribution method is presented and results on vapor-liquid equilibria, liquid-liquid equilibria and surface tension are discussed. Finally the question of how to make progress in the future is addressed.

KEY WORDS

Phase equilibria, vapor pressure, solubility, solubility parameters, group contribution methods, surface tension.

INTRODUCTION

A scientific approach to the technology of coatings is a very challenging task. Ultimately it requires an interdisciplinary application of all the main subjects of physical chemistry. It involves a variety of different equilibrium properties as well as kinetic and transport phenomena. The equilibrium states encountered in coatings belong to all the three main categories: Equilibria involving chemical reaction, equilibria involving interphases and equilibria between bulk phases. Often these different types of equilibria are in action simultaneously. Bulk phase equilibria in general involves equilibria between solid, liquid and vapor phases. In coatings the most important types of equilibria involve only liquid and vapor phases, and we shall restrict ourselves to those.

The importance of phase equilibria

It is generally recognized that phase equilibria is an important subject in coatings technology. It is first of all the key to the understanding of "solubility" of binders in solvents. The practical problem of solubility is directly related to the thermodynamic stability of a given mixture of components. The problem involves the selection of suitable solvents for a given binder - but it is more involved than that. In a typical coating formulation one often encounters several solvents and not rarely more than one binder. Typically only one of the solvents forms a homogeneous solution with the binder in question over the entire concentration range, and the phase diagram of the multicomponent system therefore contains concentration regimes where the system is thermodynamically unstable; where the mixture splits into two or even more phases. The question of solubility therefore also involves the stability of the system throughout the process of solvent evaporation, it involves the question of solvent balance. Although this problem of solvent balance is recognized, it still appears to cause confusion and problems in the application of coatings. In the application of printing inks, one often en-

counters complaints about the drying, where increased drying capacity makes no improvement. In many cases this so-called drying problem is in fact a problem related to the instability of the mixture, which leads to the formation of two liquid phases with a totally different overall rheology.

The question of stability during the entire drying process has further perspectives relating to the stability or compatibility of the final coating system. The miscibility of two or more binders and the miscibility between the binders and other non-evaporating species such as plastizicers, dispersing agents, thickeners and surfactants are of great importance for the final properties of the dried coating. Often adhesion problems develop because one or more components in a non-stable mixture migrate to the interface.

An especially interesting problem related to the question of compatibility is the prospect of formulating a two phase coating, where a homogeneous mixture of two binders and one or more solvents splits into two phases during the drying, thus creating a two layer system in only one application step (1). The design of such a system requires a fundamental understanding of the bulk phase equilibrium behaviour as well as the equilibrium behaviour of the inter-phases.

In traditional solvent based coatings thermodynamic instability is in most cases an undesired situation. In the growing area of water reducible coatings instability is however the predominant situation. The problem of phase equilibria becomes a problem of how the different species in the overall formulation are distributed between the two phases: the polymer and the water phase. The distribution of solvents and coalescing agents between the two phases has important implications as to the drying and the film-formation process (2).

In latexes the phase equilibrium problem is not qualitatively different from the solvent based systems. However when treating the so-called "semi-colloidal dispersions" the situation becomes far more complex. In these systems the binder is a polyelectrolyte which is neutralized by an acid or a base in the solution. These systems therefore in addition to the short range molecular interactions, witness long range electrolytic interactions as well as acid-base equilibria. In the last decade considerable advances have been achieved in the understanding of polyelectrolytes (3), but this still has to be "translated" or applied to the area of coatings.

The topics discussed so far all relate to equilibria between liquid phases (Liquid-Liquid-Equilibrium, LLE). Vapor-Liquid-Equilibrium, VLE, is another type of phase behaviour of importance to the coatings industry. The evaporation of solvents from a given formulation is directly affected by the VLE-properties in that major part of the drying process, where gas-phase diffusion is the rate-limiting process (4). VLE has another interesting perspective for the analytical technician, inasmuch as it forms the basis of Gas-Liquid-Chromatography. An area related to VLE is the solubility of supercritical gasses in coatings. This subject is important in estimating the protective properties of different materials (5).

METHODS FOR EVALUATING PHASE EQUILIBRIA IN COATINGS

A scientific approach to the question of evaluating phase equilibrium phenomena in coatings requires the following steps:

- 1) A model for the thermodynamic mixing functions, of which the Gibbs function is the most relevant, which is capable of describing the main features for the system at hand.
- 2) Methods for estimating unknown parameters of the model.

Model considerations

It is not the intention here to go into any detail regarding the vast topic of polymer solution thermodynamics. Several valuable references have already covered this topic (6, 11, 12).

Only a brief comment on some key points will be made. The starting point of the thermodynamics of polymer solutions is the famous Flory-Huggins expression for the Gibbs function of mixing:

$$\frac{\Delta G}{RT} = \sum_i n_i \ln \phi_i + \sum_i \sum_j \phi_i \phi_j \left(\frac{\chi_{ij}}{2} \right) \cdot \sum_i r_i n_i \quad (1)$$

From this the chemical potential may be derived. In a binary mixture

$$\frac{\Delta \mu_1}{RT} = \ln \phi_1 + 1 - \frac{\phi_1}{\chi_1} + r_1 \cdot \chi_{12} \cdot \phi_2^2 \quad (2)$$

The Gibbs function and the chemical potential is the sum of two terms: a combinatorial entropy term and a quadratic residual free energy term. The special feature of polymer solutions is embodied in the combinatorial term which on a per unit volume basis represents a much smaller entropy contribution to the mixing functions than is the case in ordinary mixtures. The residual term contains one (free energy) parameter (χ_{12}) per binary pair of components - the so-called chi-parameter.

Although the Flory-Huggins expression does indeed represent the main features of polymer solution thermodynamics, it suffers from several shortcomings. In order to fit data over wider temperature and concentration ranges it is necessary to introduce both concentration and temperature dependence into the chi-parameter. The temperature dependence of the chi-parameter often passes through a minimum. The consequence of this is that a polymer solution, which is stable at a certain intermediate temperature, splits into two phases upon cooling as well as heating. A homogeneous solution at 25°C may thus very well be unstable at, say, 75°C. Such behaviour is by no means irrelevant to coatings. It has been shown that this behaviour, as well as at least part of the anomalous concentration behaviour, is caused by the so-called "free volume" effect in polymer solutions. The polymer and the solvent have different densities, reflecting different free volumes, and this causes separate contributions to the mixing functions. These contributions may be accounted for explicitly by formulating an equation-of-state for the mixture, i.e., an equation relating pressure to volume, temperature and composition. Flory and co-workers have proposed such an equation-of-state model based on the ideas of Prigogine (6). The expression for the chemical potential according to this model is:

$$\frac{\Delta \mu_1}{RT} = \ln \phi_1 + 1 - \frac{\phi_1}{\chi_1} + \frac{P_1^* \cdot v_1^*}{RT} \cdot \left\{ 3 \frac{T}{T^*} \ln \left(\frac{\tilde{v}^{1/3} - 1}{\tilde{v}^{1/3} - 1} \right) + \frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}} \right\} + v_1^* \frac{\chi_{12}}{\tilde{v}} \cdot \theta_2^2 \quad (3)$$

where P_1^* , v_1^* and T_1^* are characteristic parameters of the pure component and $\tilde{v}_1 = v/v^*$ is the reduced volume. χ_{12} is a binary interaction parameter. At a given temperature and pressure the reduced volume is calculated from the equation-of-state:

$$\frac{\tilde{p} \cdot \tilde{v}}{\tilde{T}} = \left(\frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 1} \right) - \frac{1}{\tilde{v}^2}$$

where $\tilde{p} = P/P^*$ and $\tilde{T} = T/T^*$.

Another shortcoming of the Flory-Huggins expression is its inability to describe mixtures containing hydrogen-bonding components. These mixtures show highly non-symmetric residual free energy functions which are impossible to match with the quadratic form of the Flory χ -term. The reason for this behaviour is the tendency of the hydrogen bonds to "stick together", even at high dilutions. In other words, the different molecular segments are non-randomly distributed in the mixture. Therefore these systems require a suitable non-random mixing expression, such as the UNIQUAC (7), NRTL (8) and Wilson (9) equations. These models however require two binary interaction parameters instead of one. The UNIQUAC expression for the chemical potential is:

$$\frac{\Delta \mu_i}{RT} = \ln \phi_i + 1 - \frac{\phi_i}{x_i} + q_i \left\{ 1 - \ln \left(\sum_j \theta_j T_{ji} \right) - \sum_j \frac{\theta_j T_{ji}}{\sum_k \theta_k T_{kj}} \right\} \quad (5)$$

$$T_{ji} = \exp \left\{ -\frac{\Delta a_{ji}}{RT} \right\} \quad (6)$$

where Δa_{ij} and Δa_{ji} are the two binary parameters.

Methods for estimating parameters

All parameter estimation methods require data. In polymer solution thermodynamics there are a number of different methods for generating data. The most important are the following:

Osmotic pressure measurements. The osmotic pressure is related to the chemical potential of the solvent through $p = \Delta \mu_1 / \bar{V}_1$.

The osmotic pressure is only attainable in the dilute polymer solution, and, as all VLE-experiments, it only gives information about the solvent chemical potential.

Solvent activities can be measured directly by measuring the vapor pressure above a polymer solution relative to the pure component vapor pressure. This method is good for medium concentration ranges, but has the draw-back that the time necessary for achieving equilibrium is long and the handling of the very viscous solutions is difficult. Different thin film techniques have been developed (10), but only a limited number of systems have been measured.

Infinite dilution activity coefficients are measured on a gas chromatograph. The method is rapid and straight forward, and quite a lot of data has been generated during the last decade. The method requires temperatures well above the glass-transition temperature of the polymer, which often is well above the temperature range of interest to coatings. Extrapolation to relevant temperatures is not in general feasible.

LLE measurements. A proper LLE dataset reports pressure, temperature and composition of the coexisting phases. In polymer solutions it is difficult to obtain the polymer composition in the solvent rich phase, because it is very small. Normally therefore only cloud-points are reported. Often experiments are reported merely in terms of whether the polymer is "soluble" or "not soluble" in the solvent. This type of information only gives qualitative information, and cannot be used for estimating the model parameters.

The amount of data available in the literature of the types given above is in general limited. Data of relevance to the types of polymers used in coatings and the conditions met in the application of coatings is even less.