

67

SIGNIFICANCE OF DILUTE REGIONS

P. Alessi, M. Fermeglia, I. Kikic

Istituto di Chimica Applicata e Industriale, Università di Trieste, Trieste, Italy.

INTRODUCTION AND OBJECTIVE

According to the usual definition, infinite dilution can be defined in this way: the peculiar behaviour, under limited conditions of concentration, of a binary mixture when the concentration of one component is close to 0, while the composition of the second one is going to mole fraction equal to 1.

In a binary mixture, for obvious material balance reasons, when a mole fraction goes to zero the other one goes to 1; the extension of this concept of infinite dilution to multicomponent mixture can get rise to some ambiguity. In fact, for a mixture of n components, the infinite dilution state is not unequivocally defined, since it can be function of the composition of the components present in the mixtures. Two different situations may happen.

In the first case one can have a mixture with $(n-1)$ components at a composition close to zero and one component (J) at a composition close to 1. This situation is similar to the situation of having $(n-1)$ binary mixtures formed by the component J and the $(n-1)$ components always infinitely diluted.

In the second case, one component is present in the mixture in small quantity (close to zero) and the others $(n-1)$ in finite concentration but with a total mole fraction close to 1. This case of infinitely diluted mixture is completely different from the previous one and it is not unambiguously defined: any property of this "infinitely diluted solution" is a function of the composition of $(n-1)$ components. According to this observation, we define the infinite dilution state for multicomponent mixtures when one of the components concentration goes to the mole fraction of one. Consequently the thermodynamic behaviour of such a multicomponent mixture is described by the properties of $(n-1)$ binary mixtures and therefore we will focus the investigation only on binary mixtures.

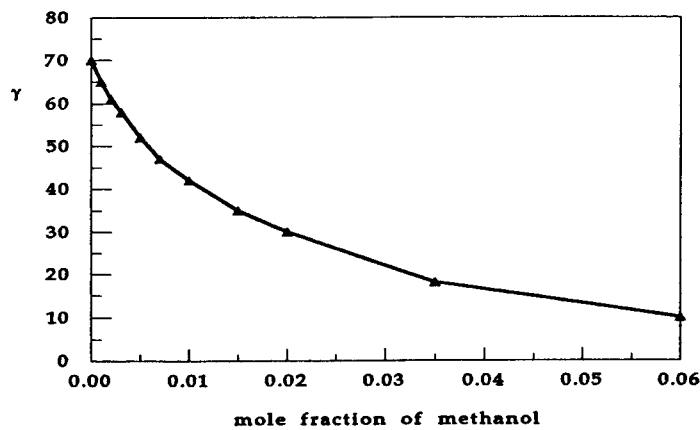


Fig. 1: Activity coefficients of methanol in n-hexane at 303 K.

An example of this representation, by considering $m_1/RT = \ln \gamma_1$ is given in figure 1 and 2. The figures evidence the validity of the criterion proposed for the definition of the infinite dilution state. By comparing these figures, one can note that the information given by the slope at infinite dilution (Figure 1) can be obtained easily in the logarithmic plot (Figure 2) through the evaluation of the intercept.

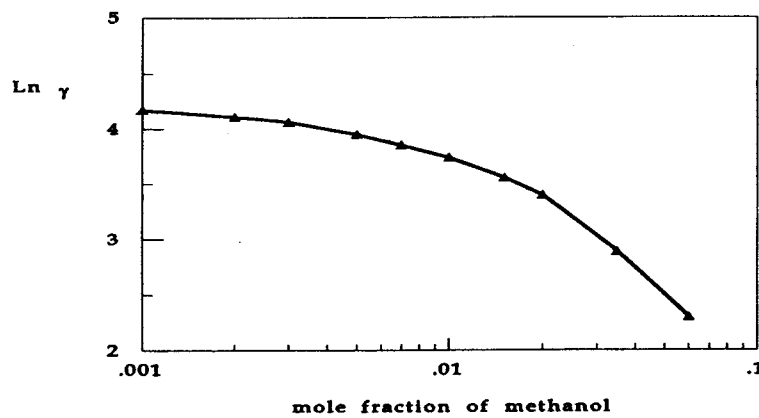


Fig. 2. Logarithmic plot for the system of fig. 1.

Figures 3 and 4 shows that some binary mixtures evidence a rather peculiar phenomenon: the activity coefficient reaches the value given by an infinitely diluted solution not for zero concentration but at a given finite, even if small, concentration. In other words the step in the logarithm plot, depending upon the components involved, is in some cases, rather wide.

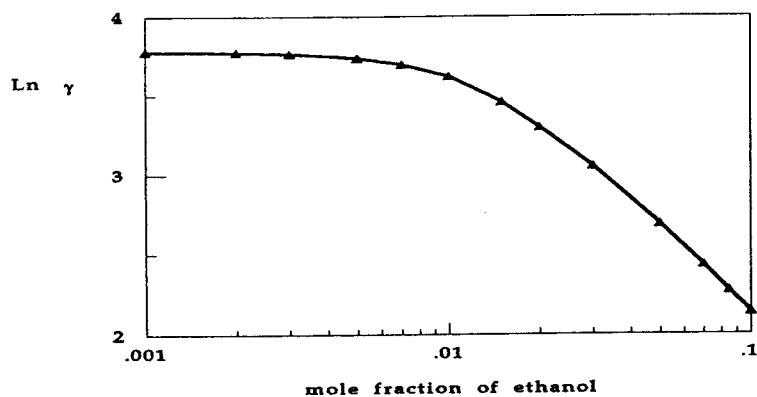


Fig. 3. Logarithmic plot of activity coefficients of ethanol in hexadecane at 298 K.

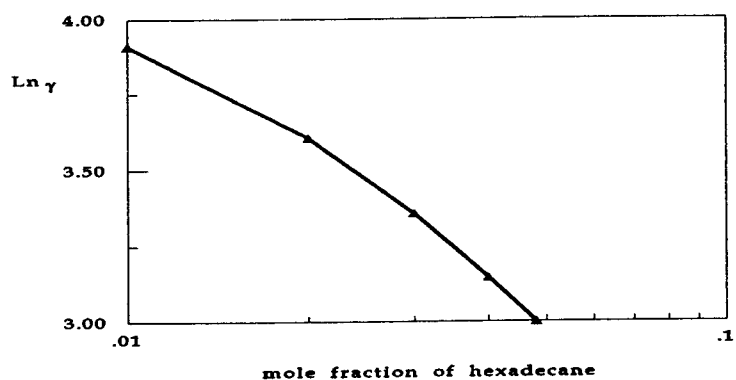


Fig. 4. Logarithmic plot of activity coefficients of hexadecane in ethanol at 298 K.

This behaviour, noted for the systems methanol/n-hexane, ethanol/n-hexadecane, can be ascribed to differences in size and/or in interaction energies of the two components and, at present, it is impossible to quantitatively predict.

It is evident that the extension of the plateau depends upon the size and interaction differences present in the mixture. From a qualitative point of view, one may say that for a mixture of similar hydrocarbons the extension of the dilute region is approximately one per cent in the dilute component, while for a solution of highly associated species, the true infinite dilution region is smaller than the 10^{-4} mole fraction and may well be as much as 10^{-6} or 10^{-7} . In the following we will focus on the consequences of this behaviour on modeling and measuring experimental data.

From the logarithmic plot mentioned above, it is possible to evaluate the extent of the infinite dilute region by evaluating the length of the plateau.

All these reasonings let us define infinite dilution for a binary mixture as the state sufficiently dilute, that solute-solute interactions are unimportant. The concentration at which this happens may vary depending upon the system considered. Extension to multicomponent mixtures is straightforward.

MODELING AND EXPERIMENTAL DETERMINATIONS

Modeling

The infinite dilution state is strictly defined in the framework of classical thermodynamics. The fugacity of the liquid phase can be written in two different forms:

$$\frac{\hat{f}_i}{x_i} = \phi_i P \quad (3)$$

$$\frac{\hat{f}_i}{x_i} = \gamma_i f_i^0 \quad (4)$$

where ϕ_i is the fugacity coefficient, γ_i is the activity coefficient and f_i^0 is the reference fugacity of component i.

When we take the limit of these expressions for $x_i \rightarrow 0$, the results are the product of the fugacity in the reference state and the activity coefficients at infinite dilution for the equation 2, while for the equation 1 is the product of the pressure and the fugacity coefficients at infinite dilution.

These equations implicitly define two thermodynamic quantities, namely the fugacity and activity coefficients at infinite dilution. The expressions which gives these coefficients as a function of temperature, pressure and concentration must be continuous and with continuous derivatives to allow the limit operation.

Equations 1 and 2 are applicable to any kind of phase considered together with the usual isofugacity criterion for the equilibrium conditions. Once the fugacity is known, classical thermodynamic relationships, written for the dilute regions, give different thermodynamic quantities such as partial excess heat of mixing, partial molar excess heat capacity, partial excess molar volume and so on. (Prausnitz et al, 1986).

The models normally used to describe the functional dependence of activity and fugacity coefficients from thermodynamic variables fulfil the condition of continuity, but fails in accounting for the interactions that occur in the infinite dilution state.

Consequently the extrapolation, which strongly depend upon the description of such interactions, may be very poor.

Additionally, there is an evidence that the substances in dense phase even if present in very small quantity create clusters (Debenedetti et al., 1989). This observation validates further the definition of infinite dilution state given above: the molecules of component 1 in the dense phase are able to see each other, to interact and to cluster even if they are in very diluted concentration. At high pressure the region of infinite dilution is probably quite narrow in respect to the low pressure situation for the same system.

Experimental determinations

Direct experimental determinations in the infinitely dilute regions need sophisticated methods and techniques because of the limiting conditions of interest.

Basically no experimental method 'a priori' fulfils the criterion chosen for defining the infinite dilution state. All the methods available in the literature require an extrapolation of at least one of the information obtained at finite, even if small, concentrations and the extent of such extrapolation to truly infinite dilution state depends upon the system investigated.

The extrapolations to infinite dilution can be done in two different ways: by extrapolating directly the measured quantities (such as pressure, temperature, molar volumes) or the calculated ones (such as activity coefficients). We recommend to rely only on methods that extrapolate directly measured quantities.

Let us consider some widely used techniques and point out the extrapolation procedure. The determination of the activity coefficients at infinite dilution with the ebulliometric method is based on the work of Gautreaux and Coates, (1985) who developed a relationship between infinite dilution activity coefficients and limiting slope of the vapour pressure curve. This slope, which is normally calculated from measurements taken at 10^{-5} mole fraction, is extrapolated to zero concentration.

For the determination of solubilities of gases or liquid in a solvent, the gas-liquid chromatographic method operates in conditions which can be approximately considered at infinite dilution. Unfortunately, also with this technique an extrapolation is needed. To evaluate the true retention time, an extrapolation of the peak to zero concentration is necessary in order to calculate the related thermodynamic quantity at 0 concentration. In this case is more difficult to state the level of dilution reached in the measurements since it depends on many factors such as quantity injected, length of the column, flow rate, stationary phase, skillness of the operator. At most true measurements may be done at concentration of 10^{-5} mole fraction.

The methods based on dilution with an inert compound also has the necessity of an extrapolation of the peak area to reach the dilute state. The same conclusions of the chromatographic method apply also in this case.

The experimental determinations of other thermodynamic quantities, such as molar volumes (Pettenati et al. 1990), heats of mixing (Roux et al. 1988), claimed as attained at infinite dilution, give, as a result, information at very dilute composition and the final step is always an extrapolation to 0 concentration of the solute.

All the techniques currently in use, included those listed above, for measuring properties at infinite dilution suffer from the fact that measurements must be done at a concentration sufficiently small to demonstrate to be at infinite dilution. For simple systems (hydrocarbons) this is easily done, but for highly interacting systems the dilution attained in the measurements is of the same order of magnitude, and in some cases even greater, than the dilute state. As a result, experiments in the infinite dilution state should be reported with an estimate of the concentration to which the real measurement has been done. This estimated data should be considered in determining the total uncertainty of the thermodynamic properties under investigation. Data available in the literature at infinite dilution (Tiegs et al, 1986) should be generally considered as extrapolated data. Users of these data should always consider possible errors which may have occurred during the extrapolation procedure.

All the difficulties reported above on experiments in the infinite dilution state allows us to state that computer simulation is actually the only 'experimental' technique suitable for the direct investigation of infinite dilution conditions. In fact these data are widely used for investigating and developing new theories of solutions.

USE OF DILUTE REGION DATA

Thermodynamic properties at infinite dilution are important to chemical engineers, from a practical and theoretical point of view.

The knowledge of the behaviour of a given mixture in the dilute region is of interest in the design of separation processes. Purification needing and recovery of valuable compounds, present in very low concentration, are classical situations where this kind of information becomes essential. Typical area of application is that involving environmental problems. One example among many others: for pollution abatement, solubilities of gas in liquids are key data for the design of absorption towers. In polymer production and use, the final step of the devolatilization of the polymer is represented by the exit of the last molecules of monomers or solvents from the bulk polymer: again we are in presence of phenomena which occur in dilute regions. For health-related products one should be interested in the last molecules intrapped in items for human use as pharmacological products, packaging of foods, medicines. Recently, the large interest in supercritical extraction processes involves the knowledge of solubilities of solids or liquids in dense fluids: for many practical applications of this technology the limit behaviour is important.

An infinitely dilute system is ideal for the application of a perturbation about the pure solvent and this can represent one possible route for the prediction of mixture properties starting from those of the pure component. In fact information obtainable in these regions are extremely important because the absence of solute-solute interactions helps to isolate the unlike solute-solvent interactions against a background of solvent-solvent interactions.

Another fundamental use involving indirectly data in the dilute region is the problem of prediction of properties in the infinite dilution state from finite concentration and viceversa.

The dependence of the fugacity from the composition has been expressed through thermodynamic models based on specific hypothesis about the nature of the interactions among the components. In general these relationships can be summarized in the form:

$$f_i = f(x_i, T, P, A_{ij}) \quad (5)$$

where A_{ij} represent binary interaction parameters which are calculated from experimental equilibrium data.

The parameters obtained from data at infinite dilution have been used for predicting the thermodynamic behaviour of the mixtures at different conditions of composition, temperature and pressure.

The use of information obtained at infinite dilution and the capability of existing models to extrapolate these properties to the full concentration range, to predict the presence of an azeotrope or the instability in the liquid phase, was studied by various Authors (Schreiber and Eckert, 1971; Loblen and Prausnitz, 1982; Nicolaidis and Eckert, 1978).

Let us consider some examples of this extrapolation. Table 1 shows some results obtained with different thermodynamic models. From the experiences derived from the investigations previously mentioned and from the few results reported one can conclude that:

- excess Gibbs energy models seem to be more flexible in the description of azeotropic conditions; equations of state describe less precisely the azeotrope;
- equations of state are able to represent mutual solubility data from infinite dilution activity coefficients better than the excess Gibbs energy models;
- for non associating systems all the models seem to give the same goodness in describing the vapour-liquid equilibrium;
- for associating systems the "traditional" models are poor and fail in describing the behaviour of the systems. The introduction of an association theory (Wenzel et al., 1982) improves the capability of the models.

TABLE 1:
Root mean squares deviations in pressure (mmHg) (RMSP) and in vapour phase composition (RMSY), mutual solubilities (X_{12}), pressure and composition of azeotrope ($P_a - X_a$) obtained with different models: UNIQUAC (Abrams and Prausnitz, 1975), UNIQUAC eff. (Nagata and Katoh, 1980), CS (Carnahan and Starling, 1969), PR (Peng and Robinson, 1976).

System	Methanol Cyclohexane		Butanol Water		Acetonitrile Benzene	
	UNIQUAC	CS	UNIQUAC eff.	CS	UNIQUAC	PR
RMSP	66.90	94.9	10.3	20.50	4.20	4.35
RMSY	0.063	0.113	0.060	0.067	0.007	0.012
X_{12}^{calc}	0.046	0.539	0.009	0.010		
X_{12}^{exp}	0.414	0.414	0.016	0.016		
X_{12}^{calc}	0.100	0.442	0.400	0.540		
X_{12}^{exp}	0.402	0.402	0.559	0.559		
P_a^{calc}					283.5	284.1
P_a^{exp}					278.1	278.1
X_{a2}^{calc}					0.529	0.528
X_{a2}^{exp}					0.530	0.530

Simultaneous composition, temperature and pressure extrapolations have been recently tested (Neau et al., 1990). Solubility data of gases in organics are used, in connection with an equation of state model, for the prediction of the solubility of the same organic in the gases at pressure and temperature (close to the critical point of the gas) at which the fluid behaves as a dense gas. From data of table 2 (mean deviations between experimental and calculated vapour mole fractions), it appears that the choice of the model does not influence the goodness of the prediction.

TABLE 2:
Mean deviations between experimental and calculated vapour mole fractions using BMVDW equation (Mansoori et al, 1971), the PR equation (Peng and Robinson, 1976) and the method of equation of state-residual functions (EOSRF) (Rauzy and Peneloux, 1986). Parameters calculated from solubility data.

Component 1	T(K)	N	$\Delta(y_1)$		
			BMVDW	PR	EOSRF
n-Heptane	310.15	21	0.0013	0.0021	0.0018
n-Decane	410.93	13	0.0010	0.0042	0.0017
Benzene	313.12	15	0.0011	0.0017	
Methanol	298.15	8	0.0020	0.0039	

In table 3 results obtained for CO₂ hydrocarbon systems are summarized. In particular mean deviations between experimental and calculated vapour mole fractions, using an equation of state based on the generalized van der Waals theory, allow the comparison between the correlation of equilibrium data, the prediction starting from solubility data only and the prediction obtained by two group contribution methods. The extrapolation results are comparable and in some cases even better than those obtained with the direct application of the model to dilute regions. This is essentially due to the fact that the systems considered are not highly interacting and the extrapolation to or from zero concentration is rather smooth.

TABLE 3:

Mean deviations between experimental and calculated vapour mole fractions using the BMVDW equation of state: comparison between correlation of equilibrium data (VLE), prediction from the correlation of solubility data (H_{21}), and prediction with group contribution methods, GCEOS (Skjold-Jorgensen, 1984) and Abdoul (1987). For Abdoul method the number of data points is slightly different.

Component 1	N	VLE	H_{21}	GCEOS	Abdoul
n-Paraffins	273	0.0053	0.0052	0.0054	0.0073
Cycloparaffins	21	0.0084	0.0066	0.0090	0.0150
Aromatics	231	0.0079	0.0078	0.0071	0.0078
Alcohols	47	0.0028	0.0023	0.0041	

Finally, thermal effects at infinite dilution, namely the variation of activity coefficients at infinite dilution with the temperature, can be used for testing the correct temperature dependence of the parameters of different models (Alessi et al., 1985).

New theories for connecting the finite behaviour with the limiting one are recently suggested by Sciamanna and Prausnitz, 1987. Not only temperature, pressure and concentration, but also phase size should be taken into account in developing new models for chemical potential.

CONCLUSIONS AND SIGNIFICANCE

The definition of the infinite dilution state for a binary mixture as a state sufficiently dilute that solute-solute interactions are unimportant is proposed. This definition is applicable to multicomponent mixtures if we consider that infinite dilution is reached when one of the components in the mixture goes to mole fraction of one.

Experimental determinations in the infinite dilution state are difficult and for highly non ideal systems (polar / non-polar or high pressure systems) the infinite dilution state may not be reached at the experimental conditions.

Liquid solution theories normally used to describe interactions at finite concentration badly performs for highly interacting systems at limiting conditions because of the inherent difficulty to represent situations such as those reported in figure 1 and 2.

Despite to all these difficulties infinite dilution data are very useful directly for the development of separation processes involving removal of traces and for a better understanding of theories for liquid solutions.

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LIST OF SYMBOLS

A	binary interaction parameter
f	fugacity
m	thermodynamic variable
P	pressure
T	temperature
x	mole fraction
γ	activity coefficient
ϕ	fugacity coefficient

Subscripts and superscripts

i	component i
°	reference state
^	mixture property
-	partial molar property
∞	infinite dilution

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