

CORRELATION OF 1-ALKANOL - N-ALKANE ACTIVITY COEFFICIENTS AT  
INFINITE DILUTION BY MEANS OF GCEOS EQUATION

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ABSTRACT

A group contribution equation of state (GCEOS) is applied for the correlation and prediction of activity coefficients at infinite dilution for systems containing n - alkane and 1 - alkanol.

The model is able to reproduce the experimental activity coefficients and the excess enthalpies at infinite dilution within the experimental accuracy.

INTRODUCTION

There is a demand of reliable experimental data on thermodynamic properties due to the extreme interest of the theoreticians in modelling, with high accuracy, the properties of non - electrolyte solutions and particularly alcohol - hydrocarbon mixtures: in fact the disparity between the polar - non polar interactions are responsible of the rather large non randomness. Interactions and size effects are phenomena which should be taken into account by a proposed model, which will naturally be tested on experimental data.

In order to do that, accurate and reliable data for these systems in the dilute regions must be available.

The study of very dilute solutions is interesting for at least two reasons: it permits to isolate the solute - solvent interaction against the background of solvent - solvent interactions; and the predominance of solvent - solvent interactions allows us to apply perturbation theories about the pure solvent in order to describe mixture properties from those of the pure components (Jonah, 1983).

DATA AVAILABLE

Tables 1 and 2 summarize the availability of binary infinite dilution activity coefficients for the systems considered (Kikic et al, 1984). The data are generally at low pressure (around 1 atm) and the temperature range (normally between 20 and 150 °C)

TABLE 1  
Summary of experimental data available, and temperature range (°C),  
for binary systems containing n - alkane and 1 - alkanol: 1-alkanol  
in n-alkane

SOLVENT	SOLUTE						
	C10H	C20H	C30H	C40H	C60H	C70H	C80H
pentane		36-66					
hexane	20	24-78	28-67	28-67	20		
heptane	20-100	41-93					
octane	20	20					
nonane		22-41					
decane		33-84					
hexadecane	25-140	25-140	25-140	25-140			
heptadecane	22-50	22-50	22-50	22-50			
octadecane	51-79	51-79	51-79	51-79			
tetracosane	60-82	51-82	51-82	51-82			
octacosane	80-120	80-120	80-120	80-120	80-123	80-123	80-123
tetracontane	84-103	84-103	84-103	84-103			
pentacontane		93-98	93-107	93-107			
hexacontane	109-123	109-123	109-123	109-123			

TABLE 2  
Summary of experimental data available, and temperature range (°C),  
for binary systems containing n - alkane and 1 - alkanol: n-alkane  
in 1-alkanol.

SOLVENT	SOLUTE				
	C5	C6	C7	C8	C9
methanol			40-70		
ethanol	20-81	20-81	38-81	25-80	27-80
propanol	20-25	20	20	25	
butanol	25		25		
hexanol					
heptanol					
dodecanol	35-60	35-60	35-60	35-60	
tetradecanol	44-76	44-75	44-75	44-75	
hexadecanol	53-94	53-180	53-94		
eicosanol	80-100		80-100	80-100	

depends on the molecular structure of the components.

From tables 1 and 2 one can conclude that: (1) data for both dilute regions have been measured for only a few binary systems and always in the case of small molecules; (2) for many systems data are completely missing, and in particular data for long chain paraffins and long chain alcohols; (3) most of the data concern small molecules infinitely diluted in large molecules, but not vice versa; (4) the accuracy of some of the data is questionable because of the wide scattering of the experimental results.

These arguments suggested us to concentrate the investigation of the dilute regions: it is necessary to obtain new accurate data (or remeasure literature data which appear to be inconsistent) using the most appropriate technique with respect to the molecular structure of the components; in addition a satisfactory model must be available for describing these properties. This paper deals with the latter problem and in particular it investigates the applicability of a group contribution equation of state in the dilute regions.

#### CORRELATION AND PREDICTION

From a practical point of view it is important to have a predictive method for extrapolating data with respect to temperature, pressure and/or molecular weight. Such methods may overcome the lack of information existing for many systems.

Models based on interaction between molecules are very accurate but do not allow extrapolation with respect to molecular weight: therefore we turned our attention to group contribution models and in particular to the group contribution equation of state (GCEOS) developed by Skjold - Jørgensen (1984) and successfully applied so far for predicting gas - solubility data. The GCEOS model should be able to represent data in a wide range of temperature, pressure and molecular weight, solving, at least in principle, the problem of extrapolation.

The reader should refer to the original paper by Skjold - Jørgensen for any detail concerning the development of the equation of state; here we point out that the model contains parameters, some of them which are calculable from pure component properties and some other which are calculated from binary data: (see appendix for the equation and the parameters).

As mentioned above, the model was developed for predicting gas - solubility data, and therefore the model parameters were mainly obtained by fitting Henry constants and high pressure vapour - liquid equilibrium data. Since we are interested in predicting limiting activity coefficients of much heavier compounds, one can expect that the numerical values of the parameters given by Skjold - Jørgensen do not work well for this purpose and need to be recalculated.

In fact, using the original parameters for the alkane - alkanol systems large mean deviations in terms of activity coefficients at infinite dilution are obtained.

In order to apply the model, new binary interaction parameters

relative to the groups considered in this investigation, have to be estimated.

For this purpose a data base is established selecting a certain number of systems from the infinite dilution activity coefficients data bank (Kikic et al, 1984), leaving out some of the systems on which to test the model.

The parameter estimation has been performed by using a modified version of the computer program developed by Skjold - Jørgensen: the modification consists in the possibility of treating excess enthalpy data in fitting and in calculation mode. The groups involved are: -CH<sub>3</sub>, -CH<sub>2</sub>, -CH<sub>2</sub>OH so that it will be necessary to operate in two steps. At first we will evaluate the interactions between CH<sub>2</sub> and CH<sub>3</sub> groups, and secondly we obtain the alkane - alkanol interaction parameters.

From the data bank more than 300 data points of activity coefficients at infinite dilution for binary alkane - alkane mixtures can be obtained. They cover a wide range of temperature and molecular weight.

Skjold - Jørgensen suggested not to use his model for very long chain molecules (above eicosane) because the soft sphere theory on which the model is based is not able to account for the size effect: only paraffines between pentane and eicosane are then used in the fitting.

Table 3 reports some of the results obtained fitting experimental data: the deviations relative to the new parameters are compared with those obtained by using the original ones. We should remark that the pure component parameters are the same as those reported in the original paper.

TABLE 3  
Deviations (DEV) relative to activity coefficients at infinite dilution of n-alkane - n-alkane systems: original parameters (ORIG), new parameters (k and  $\alpha$ ) (GINF) and new parameters (only k) (GINF1).

System	T (K)	Model	DEV
Pentane - eicosane	353 - 373	ORIG	7.87
		GINF	2.30
		GINF1	2.50
Heptane - hexadecane	304 - 324	ORIG	2.82
		GINF	1.11
		GINF1	1.20
Heptane - eicosane	324 - 353	ORIG	6.61
		GINF	2.40
		GINF1	2.65

TABLE 4  
Numerical values of the parameters obtained by fitting limiting activity coefficient data.

Groups	* k <sub>ij</sub>	<sup>1</sup> k <sub>ij</sub>	<sup>2</sup> ā <sub>ij</sub>	α <sub>ji</sub>
CH3 - CH2	.9356	-.0568	0.0	0.0
CH3 - CH2OH	.7507	-.1628	1.446	-5.175
CH2 - CH2OH	.9288	-.1523	3.627	-15.48

The inclusion of the non - randomness parameter among the parameters fitted does not influence the relative deviation and the numerical values of the other parameters. This is reasonable since the only non randomness which can occur in a mixture of alkanes is due to the difference in shape, and this is taken into account for in the repulsive term of the equation of state and not in the attractive term which contains alfa. In the following we will consider alfa parameter equal to zero.

The parameters obtained (see table 4) are slightly different from those given in the original paper.

These parameters are then used in the second step of the parameter estimation procedure: alkane - alkanol systems are now considered and the relative group parameters are calculated.

In the literature 327 data points of infinite dilution activity coefficients for n-alkane - 1-alkanol systems are reported covering a wide temperature range (20 - 125°C). They are mainly determined through the ebulliometric technique (when both molecules are small and have a similar size) or by GLC (when one component has very low vapor pressure and high molecular weight). Part of the data were used as data base, while some of the systems were left out in order to test the ability of the model in the prediction.

Table 4 reports the group interaction parameters, and table 5 shows some of the results obtained in the fitting. The comparison is made on the basis of the relative per cent deviation (DEV) defined as:

$$DEV = 100 \sqrt{\frac{\sum_i (\gamma_i^e - \gamma_i^e)^2 / \gamma_i^e}{NP}} \quad (1)$$

where NP is the total number of data points.

A relative deviation (DEV) of 5 - 10 % is not surprising because the experimental data reported in the literature are scattered. The literature reports many examples of data for the same system at the same temperature and the differences among them are typically around 6 - 10 %. Unfortunately there is no consistency test for this kind of data.

TABLE 5  
Deviations (DEV) relative to activity coefficients at infinite dilution of n-alkane - l-alkanol systems: the systems marked with an asterisk are not included in the data base.

System	T range (K)	DEV
hexane - dodecanol	308-333	4.79
hexane - hexadecanol	326-453	2.69
heptane - dodecanol	308-333	2.06
ethanol - hexadecane	298-413	8.74
propanol - hexadecane	298-413	9.79
heptane - ethanol	311-354	5.83
ethanol - heptane	311-354	7.71
ethanol - hexane	293-354	4.59
hexane - ethanol	293-354	10.58
pentane - ethanol	293-354	6.80
heptane - hexadecanol *	326-367	5.98
ethanol - octadecane *	324-352	6.21
decane - ethanol *	303-357	2.21

In this respect we can conclude that the model is able to represent the data within the experimental accuracy.

This conclusion suggests us to consider as acceptable the GCEOS model for extrapolation with respect to molecular weight in the range of compounds considered.

In order to judge about the extrapolation capability of the model with respect to temperature it is necessary to consider excess enthalpy data in the diluted region.

As suggested in a previous paper (Alessi et al,1985), this model can be used for representing excess enthalpy data: a good test for the model is then the prediction of enthalpy data from parameters obtained by fitting activity coefficient at infinite dilution.

TABLE 6  
Experimental and calculated excess enthalpies for the system ethanol(1) - n-heptane(2) at 50°C.

x1	HE exp J/mole	HE cal J/mole
.0064	143.8	148.8
.0135	269.3	284.6
.4395	968.6	1216.2
.9920	30.2	41.8
.9976	9.5	10.1

Only for very few systems we know the excess enthalpies in the infinitely diluted regions, in particular very accurate data were determined by Shatos et al.(1975) for the system ethanol - heptane at 50°C and by French et al (1979) for the system ethanol - hexadecane at 52.1 °C. Tables 6 and 7 report the experimental and calculated excess enthalpies: the agreement in the diluted regions is very good. Prediction of excess enthalpies in the finite concentration region are also reported but the results are extremely poor. Similar deviations are obtained in the calculation of excess free energies at around equimolar composition, showing that the model is not able to extrapolate with respect to temperature and composition, at the same time.

Table 7 reports also the comparison between calculated and experimental value of the excess enthalpies in the diluted region at different temperatures: the agreement is still acceptable even for large difference in size.

TABLE 7  
Experimental and calculated excess enthalpies for the system ethanol(1) - n-hexadecane(2).

x1	HE exp J/mole	HE cal J/mole	Temp K
.0010	24.6	23.9	298.15
.0022	50.7	49.1	
.0031	72.7	70.3	
.0041	95.7	93.0	
.0051	117.6	114.9	
.0061	138.7	136.8	
.0010	24.2	23.6	308.15
.0021	48.4	47.0	
.0031	72.2	70.1	
.0041	95.3	92.9	
.0051	117.8	114.8	
.0074	168.6	166.0	
.0097	215.5	215.5	
.0023	53.1	52.2	318.15
.0046	104.8	103.2	
.0068	155.3	152.9	
.0090	203.5	201.8	
.0112	249.5	249.0	
.0023	51.7	50.1	323.15
.0046	103.4	101.9	
.0068	153.7	150.3	
.0091	203.3	199.5	
.0112	250.2	246.1	
.0134	296.0	295.2	
.5757	1303.2	2807.1	
.9939	57.7	98.1	

The good capability of the model in representing thermodynamic properties in the dilute regions is mainly due to the fact that the residual combinatorial entropy obtained by the equation of state is a temperature dependent quantity because the repulsive term of the Helmholtz function is written in terms of temperature dependent hard sphere diameters.

#### CONCLUSIONS

The results show clearly that the GCEOS is applicable for calculating different thermodynamic properties in the diluted region. Particularly good results are obtained in the extrapolation of activity coefficients at infinite dilution with respect to temperature and molecular weight, filling the gaps in the available data. Furthermore the model is able to predict excess enthalpies in wide range of temperature, still in the diluted regions, within the experimental accuracy of such determinations.

The parameters given in table 4 can be slightly modified and consequently the prediction improved when more reliable data will be available.

#### ACKNOWLEDGMENT

The authors thank Steen Skjold - Jørgensen for making his computer programs available, the CNR "Progetto Finalizzato Chimica Fine e Secondaria" and Ministero Pubblica Istruzione (MPI) for the financial support.

#### APPENDIX

The total residual Helmholtz function is defined in the GCEOS model by:

$$A^r/RT = (A^r/RT)_{rep} + (A^r/RT)_{att} \quad (2)$$

The attractive term is based on the NRTL model and is defined as:

$$A^r/RT = -z/2 \sum_i^{Nc} n_i \sum_j^{Nc} v_j^i \sum_k^{Nc} \vartheta_k (g_{kj} \tilde{q}/RTV) \tau_{kj} / \sum_i^{Nc} \vartheta_i \tau_{ij} \quad (3)$$

The repulsive term is based on the Mansoori - Carnahan - Starling hard sphere model:

$$A^r/RT = 3 (\lambda_1 \lambda_2 / \lambda_3) (Y-1) + (\lambda_2^3 / \lambda_3^2) (Y^2 - Y - \ln Y) + n \ln Y \quad (4)$$

where:



$$\begin{aligned} \vartheta_i &= n_i q_i / \tilde{q} & \Delta g_{ji} &= g_{ji} - g_{ij} \\ \tilde{q} &= \sum_i^{MC} n_i q_i & Y &= (1 - \pi \lambda_z / 6V)^{-1} \\ \tau_{ji} &= \exp ( \alpha_{ji} \Delta g_{ji} \tilde{q} / RTV ) & \lambda_x &= \sum_i^{MC} n_i d_i^x \end{aligned} \quad (5)$$

The hard sphere diameter is temperature dependent and no parameters are included in the repulsive term. The attractive energy between segments is expressed by:

$$g_{ij} = K_{ij} ( g_{ii} g_{jj} )^{1/2}, \quad K_{ij} = K_{ji} \quad (6)$$

where:

$$K_{ij} = K_{ij}^* ( 1 + K_{ij}^* \ln ( T / T_{ij}^* ) ) \quad (7)$$

$$T_{ij}^* = ( T_i^* + T_j^* ) / 2 \quad (8)$$

The model contains pure group parameters which can be estimated by pure component and/or by mixture properties; in this paper we used the numerical values of these parameters given in the original paper. The adjustable parameters considered herein are therefore  $K_{ij}^*$ ,  $K_{ij}$ ,  $\alpha_{ij}$  and  $\alpha_{ji}$ .

Expressions for activity coefficients at infinite dilution, excess enthalpy and other thermodynamic properties are obtained from the expression of the Helmholtz free energy by straightforward differentiation.

#### LIST OF SYMBOLS

A <sup>f</sup>	Helmholtz free energy
K	adjustable parameter
R	gas constant
T	temperature
V	total volume
Y	hard sphere equation parameter
d	hard sphere diameter
g	attractive energy between groups
n	number of moles
q	group surface area fraction
z	coordination number
$\alpha$	non randomness parameter
$\nu$	number of groups i in the molecule j

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