

References

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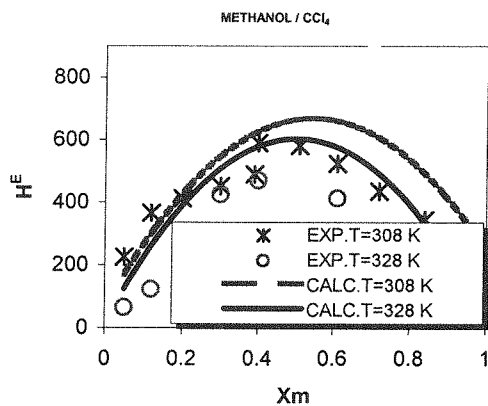


Figure (11) The excess enthalpy H^E (J/mole) for methanol / CCl_4 mixture at 308K, and 328 K.

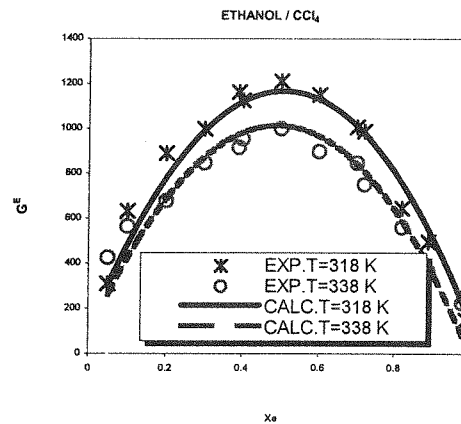


Figure (14) The excess Gibbs function G^E (J/mole) for ethanol / CCl_4 mixture 318 K and 338K. Points are experimental data form Ref. (23). Full line and dotted line were calculated using the (AA) model with chemical and physical contribution.

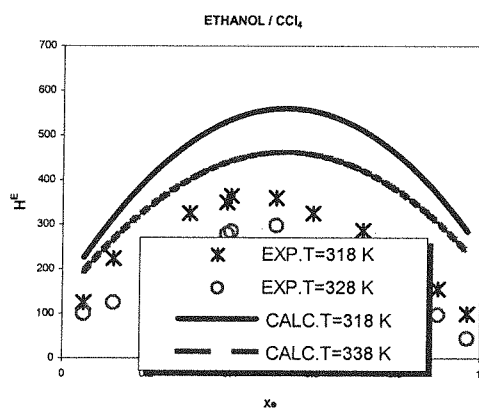


Figure (12) The excess enthalpy H^E (J/mole) for ethanol / CCl_4 mixture at 318 K and 338 K.

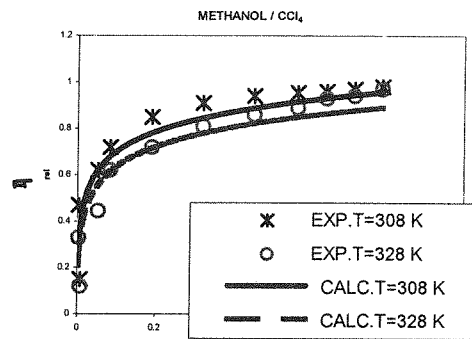


Figure (15) The relative change of the chemical shift η_{rel} for methanol / CCl_4 mixture at 308 K and 328 K. Points are experimental data from this work and lines were calculated using the (AA) model.

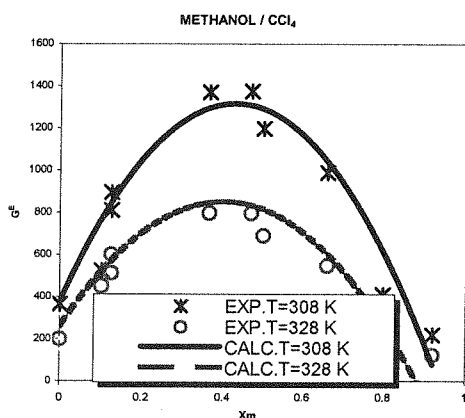


Figure (13) The excess Gibbs function G^E (J/mole) for methanol / CCl_4 mixture at 308 K and 328 K. Points are experimental data form Ref. (23). Full line and dotted line were calculated using the (AA) model with chemical and physical contributions.

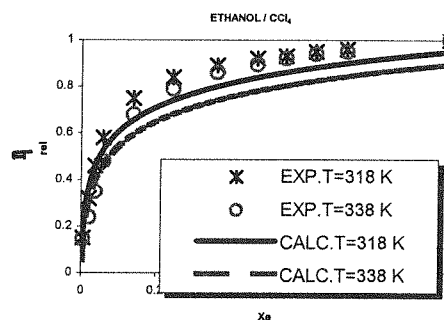


Figure (16) The relative change of the chemical shift η_{rel} for ethanol / CCl_4 mixture at 318 K and 338 K. Points are experimental data from this work and lines were calculated using the (AA) model.

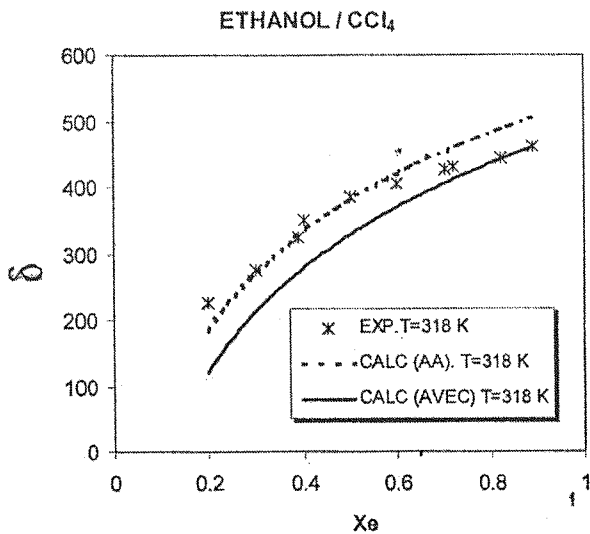


Figure (5) The observed and calculated chemical shifts δ (Hz) for ethanol / CCl_4 mixture

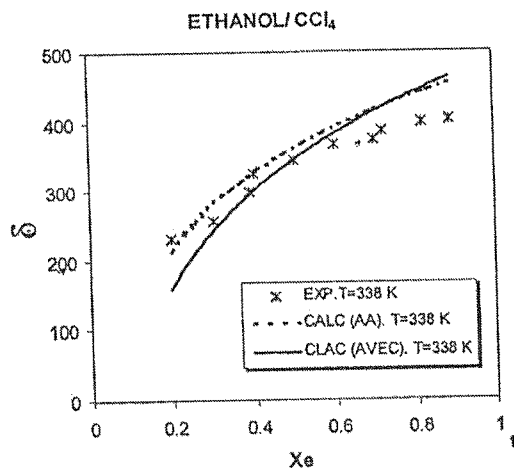


Figure (6) The observed and calculated chemical shifts δ (Hz) for ethanol / CCl_4 mixture at 338 K for AA and AVEC models.

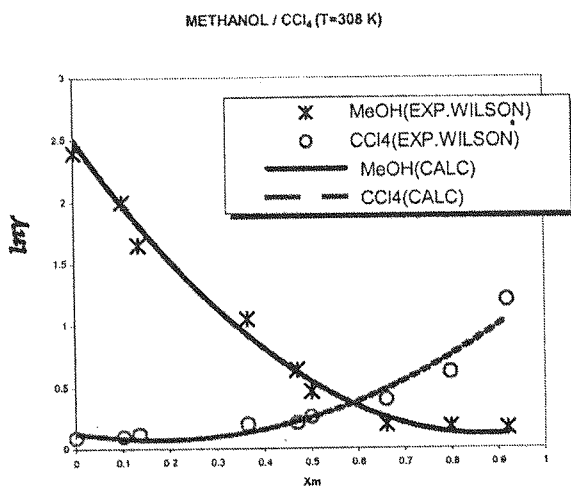


Figure (7) The activity coefficients $\ln \gamma$ of methanol and CCl_4 in methanol / CCl_4 mixture at 308K. Points represent the experimental data form Ref. (23).

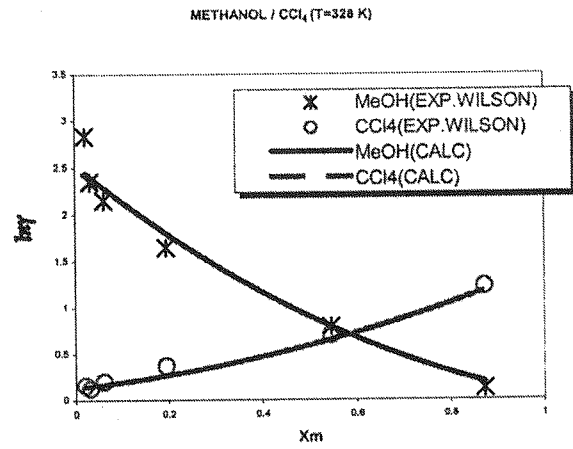


Figure (8) The activity coefficients $\ln \gamma$ of methanol and CCl_4 in ethanol / CCl_4 mixture at 328 K. Points represent the experimental data form Ref. (23).

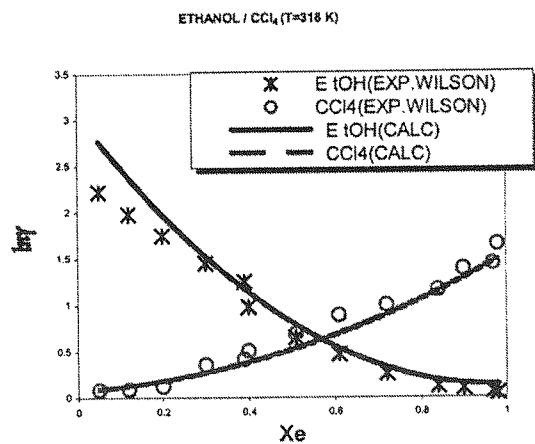


Figure (9) The activity coefficients $\ln \gamma$ of ethanol and CCl_4 in ethanol / CCl_4 mixture at 318 K. Points represent the experimental data form Ref. (23).

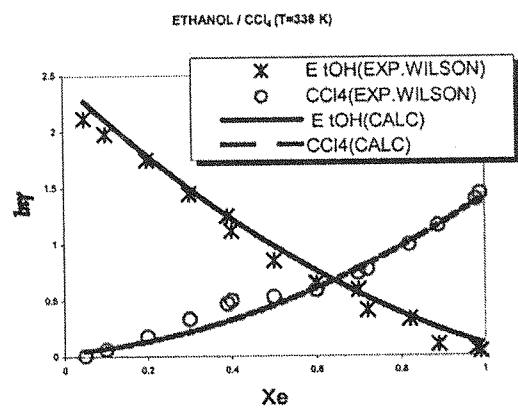


Figure (10) The activity coefficients $\ln \gamma$ of ethanol and CCl_4 in ethanol / CCl_4 mixture at 338 K. Points represent the experimental data form Ref. (23).

ϕ_{nl}	volume mole fraction of linear species
ϕ_{nc}	volume mole fraction of cyclic species
Δg_n	Gibbs Free energy change
ΔH_n	enthalpy change
ΔS_n	entropy change
$k_{nl}^{(\phi)}$	equilibrium constant of linear species
$k_{nc}^{(\phi)}$	equilibrium constant of cyclic species
L_g	adjustable parameter for linear species
C_g	adjustable parameter for cyclic species
c	chemical contribution
p	physical contribution
γ_a	activity coefficient of the alcohol
γ_s	activity coefficient of the solvent
X_1^o	monomer mole fraction in pure alcohol

X_1	monomer mole fraction in the mixture with solvent
X_s	solvent mole fraction
X_n	multimer-alcohol mole fraction
V	molar enthalpy of the mixture
H_c	molar enthalpy of the mixture
H_a^o	molar enthalpy of pure alcohol
$\delta^{(f)}$	chemical shift of free proton
$\delta^{(b)}$	chemical shift of bond proton
η_{rel}	relative change of the chemical shift
r	relative van der Waals volume
β	physical interaction parameter
σ_a, σ_s	Hildebrand solubility parameters for alcohol and solvent

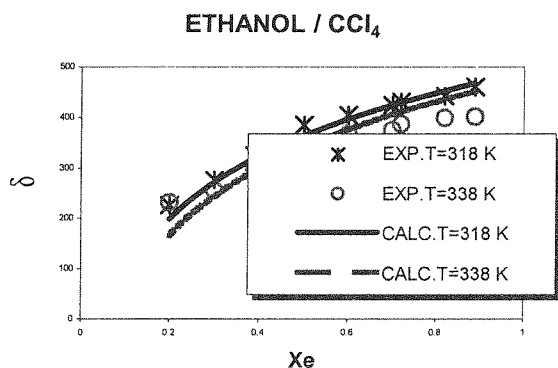


Figure (1) The observed and calculated chemical shifts δ (Hz) for methanol / CCl_4 mixture at 308 and 328 K and the extrapolations to infinite dilution.

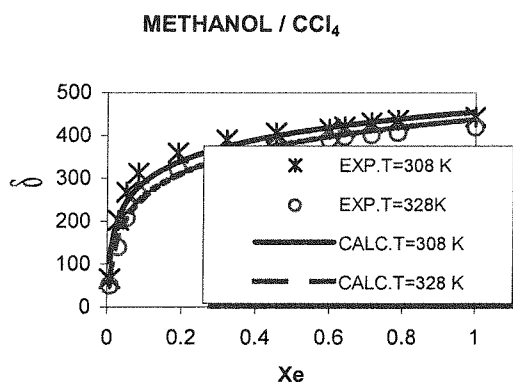


Figure (2) The observed and calculated chemical shifts δ (Hz) for ethanol / CCl_4 mixture at 318 and 338 K.

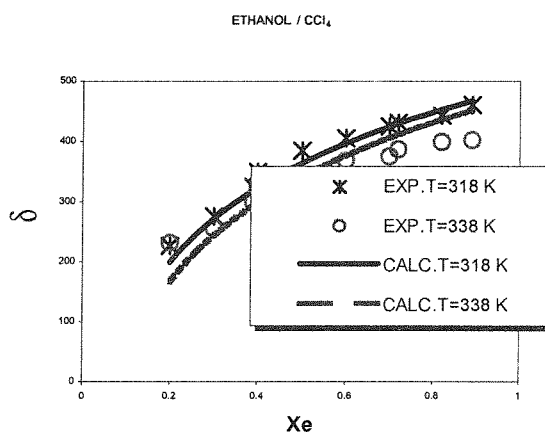


Figure (3) The observed and calculated chemical shifts δ (Hz) for methanol / CCl_4 mixture at 308 K for AA and AVEC models.

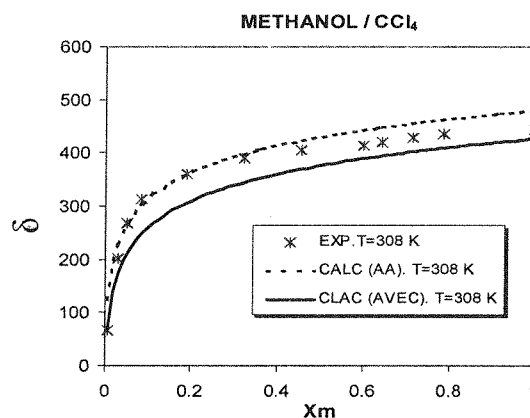


Figure (4) The observed and calculated chemical shifts δ (Hz) for methanol / CCl_4 mixture at 328 K for AA and AVEC models.

experimental data. The experimental data are listed in Table (1). In order to test the model predictability, various solution thermodynamic properties such as activity coefficient and excess enthalpy are calculated. If a model is properly realistic with the thermodynamic properties of solution, it must account for both chemical and physical interactions of the association species in the studied mixtures.

Table (1) lists the physical interaction, β , for the mixtures. Figs.(7), to, (10) and (6) show the predictions for activity coefficients of alcohol-hydrocarbon mixtures. The results show that the AA model is in good agreement with the experimental VLE data⁽²³⁾, while this is not the case with the AVEC model.

A more stringent test of a solution model, is the prediction of derivative properties such as excess enthalpy. Figs.(11) and (12) show that the differences between the two association models AA and AVEC which were not so apparent in the prediction of activity coefficient, but are quite evident in the prediction of excess enthalpies. Therefore it can be concluded that the efficiency of an association model in predicting a single thermodynamic property of solution is not a reliable assessment on the predictability of the model.

Figs.(13) and (14) illustrate the excess Gibbs function for the studied mixtures calculated by the model developed in this work. It is seen that the results are in good agreement with those calculated from VLE experimental data⁽²³⁾ by using the Wilson model⁽²⁴⁾.

The new NMR-derived quantity η_{rel} , represented by Eq. (23), is useful for the treatment of the NMR data since it is independent of any NMR-specific parameter. Another advantage of this quantity is that, it can be calculated directly from association models, providing specific information on aggregate formation through H-bonding, in the solution.

In Figs.(15) and (16), the NMR η_{rel} results, for methanol and ethanol respectively show the effect of temperature is small and therefore our previous assumptions in regard to the effect of temperature are confirmed.

Conclusion

Due to the shortcomings inherent in the AA and the AVEC models, they are not well able to predict the thermodynamic properties of associated solutions of the small alcohol molecules studied in this work. Therefore to overcome the shortcomings, as discussed in this work, the AA and the AVEC models were combined and a modified model was developed. The treatment of the NMR chemical shift data for the binary associative mixtures studied in this work indicated the effectiveness of the modified model compared with the results obtained by using, alone each of the AA or AVEC models.

Table(1) Model Parameters for Methanol and Ethanol in CCl₄.

	K	L _g	C _g	β
Methanol / CCl ₄	308	8.37	11.16	8.23
	328	7.39	9.85	8.23
Ethanol / CCl ₄	318	6.81	9.08	4.09
	338	5.91	7.88	4.09

List of symbols

k	equilibrium constant	V_s	molar volume of solvent
n	degree of association	ϕ_1	volume mole fraction of monomer species
ΔH_a^o	enthalpy change of pure alcohol	ϕ_n	volume mole fraction of n -mer species
$\Delta H_{n,n+1}^o$	enthalpy change multimers species	ϕ_a	volume mole fraction of all species
V_a	molar volume of alcohol		

$$g_p^E = \beta \phi_a \phi_s (X_a V_a + X_s V_s) \quad (28)$$

$$\beta \equiv (\sigma_s - \sigma_a)^2$$

where, β is the physical interaction parameter and is defined as the interaction energy density between solute-solvent pairs^(15,16). In Eq. (28) σ_a and σ_s are the Hildebrand solubility parameters.

Also the excess enthalpy contribution is calculated by⁽¹⁴⁾:

$$H_p^E = \beta' \phi_a \phi_s (X_a V_a + X_s V_s) \quad (29)$$

where, β' is a physical parameter which is related to β by the following equation⁽¹⁴⁾:

$$\beta' = \beta - T \frac{d\beta}{dT} \quad (30)$$

In the calculations, it is usual to assume that the second term in the above equation is small and can be neglected.

Experimental

Outline

FT-NMR spectroscopic investigations were carried out on two binary systems (methanol / CCl₄) and (ethanol / CCl₄) at temperatures of 308, 328, 318 and 338 K.

Materials and sample preparation

For all substances the highest available quality for the use in spectroscopy was HPLC grade. Methanol, Ethanol and CCl₄ were supplied by Aldrich and TMS by Merck.

For the spectroscopy investigation, liquid samples were prepared by mass and dried using a molecular sieve of type 3A.

Equipment and operation

The NMR spectroscopy was carried out on a 90 (Hz) JEOL JNM-EX FT-NMR Spectrometer. The external lock D₂O signal was used and the chemical shifts were measured against TMS. The sample cell was a Pyrex block with 5mm external diameter and the solutions was injected by means of a micro syringe.

The temperature was controlled by a thermocouple with the precision 0.1°C. The precision of the chemical shift measurements was 0.001 ppm or 0.1 Hz. The problem of chemical shift measurements in the infinite dilution was overcome by using the irradiation technique of the NMR instrument.

Results and discussion

The results of chemical shift measurements of the protons in OH-groups in methanol and ethanol in solution with CCl₄ and their relative changes as given by Eq. (23) are shown in Figs. (1) to (6)

The chemical shifts at finite dilution were obtained by extrapolation of the measured data. The figures show that the results are in good agreement with the corrected model of AVEC presented in this work. The parameter values of L_g and C_g of Eqs. (6) and (7) estimate and then calculate constant equilibrium and the activity coefficients of mixtures at different temperatures then they would be acceptable if the results are not much different with

$$\Delta\delta_{n,obs} = \delta_{n,obs} - \delta_n^{(f)} = \left(\frac{n^{(b)}}{n_n}\right)D = \left[1 - \left(\frac{n^{(f)}}{n_n}\right)\right]D \quad (22)$$

$$D \equiv \delta_n^{(b)} - \delta_n^{(f)}$$

The relative change of the chemical shift η_{rel} can be defined for the two protons, free and hydrogen bond, as follows:

$$\eta_{rel} = \frac{\Delta\delta_{obs}}{\Delta\delta_{obs}^o} = \frac{\delta_{obs} - \delta_{obs}^\infty}{\delta_{obs}^o - \delta_{obs}^\infty} \quad (23)$$

The relative change of the chemical shift is a dimensionless quantity normalized to the (0,1) interval and can be directly evaluated from the observed chemical shifts⁽¹³⁾:

$$\eta_{rel} = \frac{1 - \left(\frac{n^{(f)}}{n}\right)}{1 - \left(\frac{n^{(f)}}{n}\right)^0} \quad (24)$$

For the athermal association models outlined above, the relative size of the "free" proton populations can be expressed as follows:

$$\frac{n^{(f)}}{n} = \frac{\sum(\phi_n/n)}{\phi_a} = \left(\frac{\phi_n}{X_a} - \frac{\phi_s}{r}\right)\phi_a \quad (25)$$

which upon substitution into Eq. (24) gives:

$$\eta_{rel} = \frac{1 - \left(\frac{\phi_n}{X_1} - \frac{\phi_s}{r}\right)/\phi_a}{1 - \left(\frac{\phi_n^o}{X_1^o}\right)} \quad (26)$$

where r is the relative van der Waals volume scaled according to the following equation⁽¹⁷⁾:

$$r = \frac{V_a}{V_s} \quad (27)$$

In this work the modified association model developed by combining the Athermal Association model (AA) represented by Eqs. (22)-(26), and the Association with Variable Equilibrium Constant model (AVEC) represented by Eqs. (6)-(8), are used to study the self-association due to hydrogen bonding of alcohols in non-polar solvents.

In the case of using polar solvents which may be involved in hydrogen bonding the model can be extended according to the method suggested by Tkadlecova et al.⁽¹³⁾

It is worth noting that in the calculations, in this work, the physical contribution on g_p^E is given, by an one-parameter equation, as suggested by Scatchard⁽²²⁾:

$$H_c^E = H_c - X_1 H_a^o \quad (16)$$

where, H_c is the molar enthalpy of the mixture given by:

$$H_c = \frac{\Delta H_a^o \sum_n (n-1) X_n}{1 + \sum_n (n-1) X_n} \quad (17)$$

and X_n are the mole fractions of the corresponding multimers. H_a^o in Eq. (17) is the molar enthalpy of pure alcohol.

The equilibrium constant and enthalpy of hydrogen bonding are related by the well-known van Hoff's equation:

$$\frac{d \ln K_n^{(\phi)}}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H_a^o}{R} \quad (18)$$

H-NMR spectroscopy and association model

NMR is particularly useful in the study of weak intermolecular complexes involving specific H atom and can also be carried out in various solvents. While in the other spectroscopic methods such as IR, in the self-association system, each H-bonded species can in principle be individually distinguished⁽²¹⁾, in NMR spectroscopy an average signal for all the species is observed.

The formation of a hydrogen bond decreases the local electron density and causes change in the electromagnetic shielding of the proton involved⁽¹³⁾ and some properties of solution, for example viscosity and boiling point, are increased. In NMR spectroscopy the hydrogen bonding causes a change in the chemical shift and then the observed chemical shift is the average sum of free protons and those involved in hydrogen bonding.

Let $\delta^{(f)}$ be the chemical shift of free proton and $\delta^{(b)}$ the chemical shift of bound proton, then the following equation, which is known as the weight average or population average is hold⁽⁹⁾:

$$\delta_{obs} = \left(\frac{n^{(f)}}{n}\right)\delta^{(f)} + \left(\frac{n^{(b)}}{n}\right)\delta^{(b)} \quad (19)$$

The weights are the relative sizes of the respective populations $n = n^{(f)} + n^{(b)}$.⁽¹³⁾
The chemical shift of monomer at infinite dilution of solution is represented as:

$$\lim_{x_a \rightarrow 0} \delta_{obs} \equiv \delta_{obs}^\infty = \delta_a^{(f)} \quad (20)$$

$$\delta_{obs(x_s=1)} \equiv \delta_{obs}^0 = \delta_s^{(f)} \quad (21)$$

The chemical shift of multimer is given by:

related⁽¹²⁾:

$$C_g = \frac{4}{3}L_g \quad (8)$$

The temperature dependence of the equilibrium constant is given by Eq. (5) where ΔS_n is the entropy of hydrogen bonding formation of alcohol molecules which is assumed to be independent of the temperature⁽¹⁸⁾.

The Excess Thermodynamic Functions

The equilibrium constant is used to calculate the properties of solution and is determined by fitting NMR chemical shift data to a specific association model. The excess Gibbs energy is defined as:

$$g^E = g_c^E + g_p^E \quad (9)$$

where, the subscript c and p are respectively for chemical and physical contributions. The chemical contribution g_c^E is related to the activity coefficients:

$$g_c^E = RT(X_a \ln \gamma_a + X_s \ln \gamma_s) \quad (10)$$

In the Athermal Association model (AA), the activity coefficient of the alcohol γ_a and the solvent γ_s is derived by the method of Brandane⁽¹⁹⁾ and is expressed as:

$$\ln \gamma_a = \ln\left(\frac{\phi_1}{X_a \phi_1^o}\right) + \frac{\phi_1^o}{X_1^o} - \frac{\phi_1}{X_1} \quad (11)$$

$$\ln \gamma_s = \ln\left(\frac{\phi_s}{X_s}\right) + 1 - \frac{\phi_s}{X_s} \quad (12)$$

where, X_1^o is the monomer mole fraction in pure alcohol, and X_1 is the mole fraction of monomer in the mixture with solvent. In general, multimer-alcohol mole fraction X_n and solvent mole fraction X_s are given by:

$$X_n = \frac{\phi_n V}{n V_a} \quad (13)$$

$$X_s = \frac{\phi_s V}{V_s} \quad (14)$$

where, the molar volume of solution (V) is given by⁽²⁰⁾:

$$\frac{1}{V} = \frac{\phi_s}{V_s} + \sum_n \frac{\phi_n}{n V_a} \quad (15)$$

The chemical contribution to the excess enthalpy is expressed as¹³:

that the equilibrium constant shouldn't be expressed in terms of mole fraction ¹³ and according to the Flory's lattice model for solution polymerization.^(15,16)

$$K_{n+1} = \left(\frac{\phi_{n+1}}{\phi_n \phi_1} \right) \frac{n}{n+1} = \left(\frac{C_{n+1}}{C_n C_1} \right) \frac{1}{V_a} \quad (1)$$

where, $n \geq 1$, V_a is the molar volume of alcohol and ϕ_1 , ϕ_n are the volume mole fractions of monomer and n -mer respectively.

The monomer volume fraction involved in the relationships given above is obtained by solving simultaneously equilibrium and balance equations. In particular, the monomer volume fraction ϕ_1 and that of n -mer (ϕ_n) are related by the following equation:

$$\phi_a = \phi_1 + \sum_{n=2}^{\infty} (\phi_{nl} + \phi_{nc}) \quad (2)$$

where, ϕ_{nl} and ϕ_{nc} are respectively the volume fraction of linear and cyclic species.

Eq. (1) can be written for linear species as:

$$\phi_{nl} = \frac{n-1}{n} \phi_1^n K_{nl}^{(\phi)} \quad (3)$$

and for cyclic species as:

$$\phi_{nc} = n \phi_1^n K_{nc}^{(\phi)} \quad (4)$$

for n -mer formation the following well known thermodynamic equation can be written:

$$\Delta g_n = -RT \ln K_n^{(\phi)} = \Delta H_n - T \Delta S_n \quad (5)$$

where, according to the association model assumption $K_n = K_{n+1}$, and the other symbols are: Δg_n is the Gibbs free energy change and ΔH_n , ΔS_n are respectively the enthalpy change and entropy change. For linear species $K_{nl}^{(\phi)}$ can be expressed as ⁽¹²⁾:

$$\ln K_{nl}^{(\phi)} = \frac{L_g}{n-1} \quad (6)$$

where L_g is an adjustable parameter. For cyclic species similar equation can be written:

$$\ln K_{nc}^{(\phi)} = \frac{C_g}{n} \quad (7)$$

where, in a linear species there are $(n-1)$ hydrogen bonds, and for a cyclic species, the end protons are not free. In Eq. (7) C_g is an adjustable parameter. It is worth noting that equations. (6) and (7) are based on the logarithmic form of Eq. (5) for the formation of linear and cyclic complexes respectively, where, there are n hydrogen bonding reactions in forming a complex containing n -mer. It can be shown that the two parameters are not independent but inter-

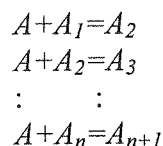
- temperature dependence of the excess enthalpy⁽¹²⁾.
- ii- The Linear Association with Cyclic Trimer (LACT) model⁽¹²⁾ which was developed for the cyclic trimer. An unique equilibrium constant is assigned to cyclic complex formation and all higher order complexes in the solution are considered linear with equally probability. This model is able to predict activity coefficients quite well and is able to predict the correct composition and temperature dependence of excess enthalpy. However, the LACT model fails to predict the liquid-liquid coexistence curve for methanol system.
 - iii- The Association with Variable Equilibrium Constant (AVEC) model is based on the assumption that as temperature of the solution increases, the oligimers breakdown to form the more stable complexes, the trimer or tetramer. The unique feature of this model is that the probability of forming the various species is no longer equal but depends on the size of the complex. But this model is not able to fit well with experimental result of small alcohols (methanol and ethanol) and that it can be combined with the Athermal Association (AA) model⁽¹³⁾ to fit well with experimental data in the case of small alcohol.
 - iv- There are also a number of other association models that could be used to predict solution behaviour such as trimer only or tetramer only, but they have limited application. Often the predication of activity coefficient by these models is poor and predication of more sensitive solution properties such as excess enthalpy or LLE may be even worse⁽¹²⁾.

In this work NMR spectroscopy results are used to study the molecular associations due to hydrogen bonding of methanol and ethanol in the binary solutions with solvent CCl₄. The thermodynamic properties of the mixtures are calculated by using two models (AVEC-AA) and the accuracy of them in predicting the thermodynamic properties is examined in the light of the results obtained.

Association models

That association models can be used to calculate thermodynamic excess functions by NMR result. The essence of the theory of the models is as follows:

- 1- All alcohol species exist in the mixture.
- 2- All association chain reactions have an equilibrium constant that is independent of association number n .
- 3- The linear chain, hydrogen bonded polymers formed by reactions of the type:



- 4- There are physical interactions between all polymer species and the no ideality in the liquid mixture is due to the existence of this species.
- 5- The temperature dependence of equilibrium constant H^E is such that the enthalpy of formation of a hydrogen bond is independent of the temperature and degree of association n .^(13,14)

$$\Delta H_{n,n+1}^{\circ} = \Delta H_a^{\circ}$$

where, ΔH_a° is the enthalpy change of pure alcohol and H^E is the enthalpy change of multimer species. Those models which involve this assumption is known as the Athermal Association models (AA).

- 6- The equilibrium constant is expressed on volume fractions. Flory's treatment clearly shows

Experimental and Theoretical Study of Self-Association of Light Alcohols in Chloroform by NMR Spectroscopy

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Abstract

The thermodynamic properties of OH-bonding solutions have been investigated by NMR spectroscopy for two binary systems of alcohols (Methanol and Ethanol) in CCl_4 at temperatures 308, 328, 318 and 338 K. A modified model based on the two previous models Athermal Association model (AA) and Association with Variable Equilibrium Constant model (AVEC) have been used for fitting the experimental data.

The activity coefficients and the excess thermodynamic properties (G^E , H^E) of associated alcohols were calculated by the proposed modified model and the results were compared with data of vapor pressure measurement. This comparison indicated that the proposed model is capable of treating the NMR data to obtain the thermodynamic properties of the associated solutions.

Introduction

The spectroscopic measurements are used to study the molecular interactions in the mixtures and these measurements are led to several models for calculation of thermodynamic properties of these mixtures. In this respect the interactions of solute-solvent and self-association have been of special interest⁽¹⁾.

The hydrogen bonding among molecules is known as the main factor in the molecular association in the mixture. Experimental methods have shown that hydrogen bonded molecular complexes of polymer like species are formed due to the molecular association.⁽²⁻⁸⁾

Nuclear Magnetic Resonance (NMR) spectroscopy is one of the major methods used to study molecular complexes. Gutowsky and Saike⁽⁹⁾ have shown that the observed chemical shift in a hydrogen bonded mixture is a weight average of hydrogen bonded and free proton which are in equilibrium.

Several models have been proposed to treat the NMR results and to obtain the thermodynamic properties of the hydrogen bonded mixture.⁽¹⁰⁻¹²⁾ The most commonly used models are:

i- The Continuous Linear Association Model (CLAM) used by Krestchmer and Wiebe⁽¹⁰⁾ and Renon and Prausnitz⁽¹¹⁾ for alcohol-hydrocarbon mixtures were restricted to formation of linear species only, all with equal probability of forming. The CLAM model predicts activity coefficients well over the entire composition range but it is not able to predict the