

EXCESS THERMODYNAMIC PROPERTIES CALCULATIONS FOR ALCOHOLS IN INERT SOLVENTS BASED ON FOURIER TRANSFORM INFRARED SPECTROSCOPY MEASUREMENTS

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Abstract

Self-association of alcohols; including ethanol, methanol, cyclopentanol and octanol in separate mixtures with inert solvents have been studied using FT-IR spectroscopy. Except for the band at 3640 cm^{-1} in the IR spectrum of the alcohols which is due to the monomer species, the presence of other bands in the region of stretching vibrational frequencies of OH ($3100\text{--}3700\text{ cm}^{-1}$) are attributed to the higher associated species such as dimer, trimer and multimers. Association models of such as trimer, continuous linear association model, linear association with cyclic trimer (LACT) and dependent equilibrium constant model (DECM) have been used for treating the IR Spectroscopy results. The calculations indicated that the dominant species in the studied concentration range of alcohols is the trimer. The evaluated association constants in the best-fitted model (timer or LACT) were utilized to obtain the excess properties such as h^E , g^E and activity coefficients for the mixtures.

Keywords: Excess properties; Activity coefficient; Associative fluids; FT-IR; Alcohol + inert solvent; Association constant; Self-association

Introduction

Phase equilibrium data for mixtures and their dependence on pressure, temperature and other thermodynamic variables are essential in understanding of natural and industrial phenomena. The availability of data on the phase equilibrium properties of mixtures are

vital in chemical industries for design and optimization purposes, in the processes such as separation, purification and pollution control. In this respect the mixtures with hydrogen bonding among the molecules present in the mixtures are of special interest. Such mixtures, in general, are called associated mixtures. A mixture of an alcohol in an inert solvent is a common

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example of an associated mixture in which different associated species are present, due to the formation of hydrogen bonds among the alcohol molecules [1]. These species are known to be responsible for deviation of these mixtures from ideal behavior. Therefore prediction of thermodynamic properties is an important task to understand the behavior of associated mixtures.

Most theories for mixtures have been developed in attempt to explain the deviations from ideal behavior in terms of intermolecular forces. The regular solution theory [2], the non-random two liquid mixtures [3] and the Wilson theory [4,5] can be named in this respect. However these theories fail when they are applied to the associated mixtures.

The chemical theories were presented after the pioneering work of Dolezalek [6] and have been successful in considering the behavior of associated mixtures. The essential assumption in the chemical theory is that; the entire non-ideal behavior is due to the presence of the associated species that are formed by chemical interactions. However it seems that a combination of both physical and chemical theories can be more successful in a proper treatment of the associated mixtures.

Aghamiri *et al.* [7] have introduced a generalized chemical association theory for calculation of thermodynamic properties. They have presented an analytical solution for the theory when applied to the binary associating fluid mixtures. In a subsequent paper [8] they used the theory to calculate the conformal parameters for a conformal associating mixture and proposed a procedure for computing the parameters of cubic equation of state for associating fluid mixtures.

Various experimental methods can be used for evaluating molecular associations and among them we can name the spectroscopic [9-14], dielectric [15], dipole moment [16] and neutron scattering methods [17].

Theoretical methods such as statistical thermodynamics, quantum mechanics, monte-carlo simulation [18] and chemometrics [19,20] also can be used. Other physical properties of mixtures; including melting point, boiling point, heat of vaporization and solubility are influenced by the molecular association and can be utilized to study the molecular association. There are also reports on the effect of molecular associations on the kinetics of reactions involving alcohols [21].

Among other methods, spectroscopy is a powerful tool to study the associated mixtures. Spectroscopy is an inexpensive and fast method and provides direct quantitative information about the kind of existing species and their concentrations in the mixture. We can

name IR [9-13] and NMR [14] as the most effective spectroscopic methods.

In this research IR spectroscopy is used for evaluating the molecular associations, which are due to the hydrogen bonding of alcohol molecules in an inert solvent.

Due to the hydrogen bonding a vibrational band in IR spectrum; in the region $3100\text{--}3700\text{ cm}^{-1}$ is observed. The OH band of alcohols consists of peaks that can be attributed to the monomer, dimer, trimer, tetramer and linear or cyclic n-mers. As the intensity of the absorptive spectrum at the characteristic frequency of OH bond is proportional to the concentration of the species, the measurements of the peak intensity as a function of concentration of the mixture can lead to valuable information about the existing species in the mixtures. Using these data the proper association model that is consistent with the experimental data is chosen and is used for calculating the thermodynamic properties.

Experimental

The impurities in alcohol (Aldrich 99.9%), mostly water were removed by distillation, passing through molecular sieve column and adsorption by CaO. Carbon tetrachloride and hexane, spectroscopic grade (Merck 99.9%), were used without further purification since they are not water absorber and their spectra do not show absorption peaks around those of water (3680 cm^{-1}).

The solutions of alcohol in solvent were made by mass measurements using an analytical balance with accuracy of 0.0001 g. In spectroscopic measurements the samples were put in two-NaCl-window demountable liquid cell (Buck Ins. Co.). The cell thickness was 0.25 mm. The spectra were obtained by the IR spectrometer (Buck Ins. Co.). The output signal from detector was processed by utilizing the (Grams/IR+) software. The temperature was controlled with the accuracy of 0.1°C .

Spectroscopic Results

(a) IR Spectra

Luck and Schrems [22] have attributed the peaks in $3200\text{--}3700\text{ cm}^{-1}$ of IR spectra of ethanol to the dimer and multimers. Trucker and Becker [23] have studied the IR spectrum of mixture t-BuOH in hexadecane. They observed three bands with the frequencies of 3624 , 3510 and 3350 cm^{-1} . They also mentioned the possibility of observing a fourth peak at 3400 cm^{-1} . The observed peak at 3624 cm^{-1} is due to the vibration

stretching of the monomer, but there are contributions from the other groups located at the end of the linear chain formed by the associated alcohol molecules. The bands at 3510 and 3350 cm^{-1} are due to the formation of dimer and multimer, respectively.

In a study by Martinez [12,13] on a mixture of alcohols and alkanes, the shape of the original band at 3360 cm^{-1} and the shoulder-bands at 3640 and 3628 cm^{-1} have been attributed respectively to the monomer and to the other two different species. The wider band at 3350 cm^{-1} and shoulder-bands at 3450, 3280 and 3205 cm^{-1} are due to the cyclic-multimer. Draye *et al.* [8] have reported the following vibrational frequencies; monomer (3600 cm^{-1}), cyclic dimer (3495 cm^{-1}) linear dimer, and linear polymer (3340 cm^{-1}).

In our spectroscopic measurements on the alcohols in mixtures with inert solvents, similar results were obtained. Figure 1 shows the spectrums of ethanol in carbon tetrachloride. As it is expected and seen in this figure, there are three peaks at 3100-3800 cm^{-1} which are shown by A, B and C.

Schwager [11] has reported a difference between peaks due to free OH group and those involved in hydrogen bonding; that is with increasing the temperature, the surface area under the free OH peak increases whereas for the hydrogen bonding the area of OH peak decreases. This means that with increasing the temperature, the number of hydrogen bonding species in the mixture decreases.

(b) Concentration Determination

The concentration of different associated species can be determined by IR data.

According to the Beer-Lambert law for an absorption peak we have:

$$A = \varepsilon l C \quad (1)$$

where A is absorbance, ε is molar absorbance, C is molar concentration and l is cell length.

(c) Concentration of Monomer

If the maximum height of peak and the area under the peak are equal, they should be linearly proportional to the concentration of alcohol. However, the study of Draye [9] on self-association of cyclopentanol in toluene and acetonitrile does not show such a trend.

Dubec [30] observed that the area under the free OH bands is due to the total number of free OH bonds. This consists of OH in monomers and linear multimers. The maximum absorption intensity is only due to OH in monomers. This can be related to the fact that the band corresponding to the free OH group at the end of the n -mer chain is located in lower energy region and the band corresponding to hydrogen bonding is located at higher energy. Therefore the maximum peak in the OH band can be taken for the monomer concentration C_1 and according to the Beer-Lambert law we have:

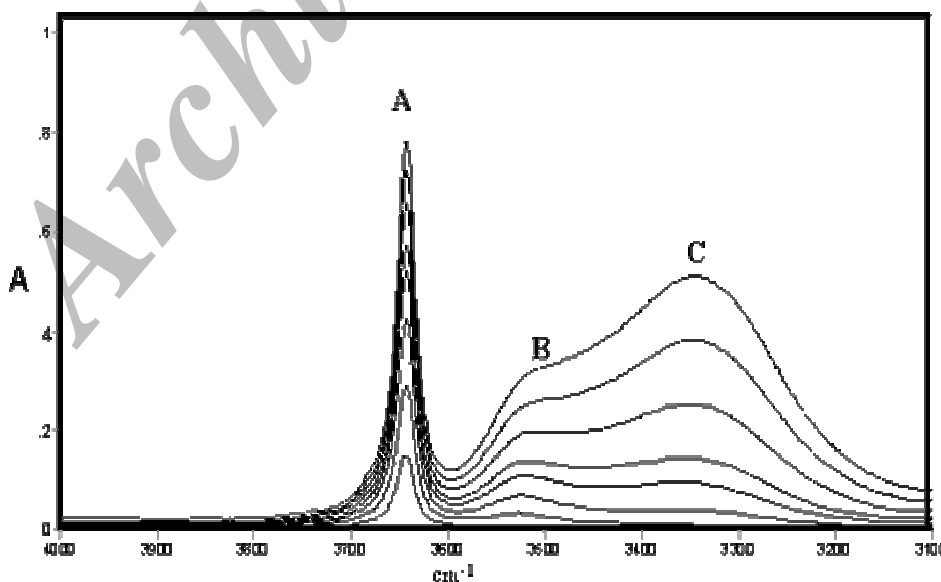


Figure 1. The IR spectra of ethanol with different concentrations in ethanol+ CCl_4 mixture at 25°C.

$$C_1 = \frac{A_{fOH}^{\max}}{l \varepsilon_{fOH}^{\max}} \quad (2)$$

The true absorbance of OH bond is obtained by deconvolution method. Then by an especially developed software the values of ε_{fOH}^{\max} are calculated at any concentration. At very low concentration of alcohol ($C_a \rightarrow 0$) the value of ε_f for free OH can be evaluated as: $\varepsilon_f = A_f / l C_a$, where A_f is the absorbance of free OH bond and is evaluated by extrapolation to zero concentration of alcohol. Its worth noting that at very low concentration the alcohol is present in the form of monomer.

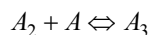
Table 1 reports the ε_f values for the alcohol used in this study.

Table 1. Molar absorbance values (L/(mol.cm)) calculated by extrapolation from IR spectra of monomer peaks for different alcohol+inert solvent mixtures

System	T (K)	ε_f
Methanol+Hexane	298	2.60
Ethanol+Hexane	298	1.80
Cyclopentanol+Toluene	328	65.01
Ethanol+CCl ₄	313	5.76
Ethanol+CCl ₄	323	5.45
Ethanol+CCl ₄	332	5.19
Octanol+CCl ₄	298	60.08

Modeling

The aim of this work is to determine which association model is more appropriate for treatment of a mixture of an alcohol in an inert solvent. In general, a number of associated species are formed due to the hydrogen bonding of alcohol molecules, which can be shown by the following reactions;



...



The equilibrium constant for Equation (4) can be expressed in terms of molarity(C) as:

$$K_{C_{n+1}} = \frac{C_{n+1}}{C_n C_1} \quad (5)$$

which in terms of volume fraction ϕ has been represented by the following equation [24]:

$$K_{\phi_{n+1}} = \frac{\phi_{n+1}}{\phi_1 \phi_n} \cdot \frac{n}{n+1} = K_{C_{n+1}} \cdot \frac{1}{V_a} \quad (6)$$

where, V_a , is molar volume of alcohol.

As it is seen from equation (6), there is no contribution from physical bonds in equilibrium constant and therefore it can be considered as a pure chemical model or a simplified model derived from general physico-chemical theory of molecular associations. In this model the equilibrium expression for dimer, trimer and polymer species can be written as:

$$C_2 = K_2 C_1^2 \quad (7)$$

$$C_3 = K_3 C_2 C_1 = K_3 K_2 C_1^3$$

$$C_n = K_2 \dots K_n C_1^n$$

and the molar balance equation is:

$$C_a = C_1 + 2C_2 + 3C_3 + \dots + nC_n \quad (8)$$

By substituting from equation (8) in (9) we have:

$$C_a = C_1 + 2K_2 C_1^2 + 3K_2 K_3 C_1^3 + \dots + nK_2 K_3 \dots K_n C_1^n \quad (9)$$

The equilibrium constant K_i can be expressed in terms of thermodynamic quantities by the well-known equation:

$$\Delta g_i^o = -RT \ln K_i = \Delta h_i^o - T \Delta s_i^o \quad (10)$$

where K_i , Δg_i^o , Δh_i^o and Δs_i^o are respectively the equilibrium constant, molar Gibbs function, molar enthalpy and entropy change for the species i .

There are many unknown parameters in Equations (7) to (10). Therefore simplifications are needed to make them applicable for the numeric calculations. In a number of models it is assumed that only one kind of associated species, for example, monomer-trimer or monomer-tetramer is present in the mixture [25]. In other models the presence of some special species is assumed [26]. Also there are some models based on the assumption that all kinds of species are present in the mixture but their equilibrium constants are not independent [27].

However, the detailed study on the hydrogen bonding mixtures has shown that, the presence of a number of species is certain in the mixture. Therefore in the proposed models it is desired to take all kinds of species in the mixture into account. On the other hand, the studies based on IR, NMR and vapor pressure measurements have shown that the dominant species in the alcohol solvent mixture is the trimer [23] and the

presence of dimer can be ignored.

In what follows various models are discussed:

CLAM

Continuous linear association model (CLAM) is a simple model in which it is assumed that all protons have equal probability of taking part in the association and therefore considers linear structure for the associated species. This model was primarily proposed by Flory [24] and was used by Kretschmer [28] and Renon, Prauznitz [29] for molecular association of alcohols. The mass balance equation in this model is:

$$C_a = C_1 + 2KC_1^2 + 3K^2C_1^3 + 4K^3C_1^4 + \dots + nK^{n-1}C_1^n \quad (11)$$

This equation can be written as:

$$C_a = \frac{1}{K} \sum_{n=0}^{\infty} n(KC_1)^n = \frac{1}{K} \cdot \frac{KC_1}{(1-KC_1)^2} = \frac{C_1}{(1-KC_1)^2} \quad (12)$$

The parameter K can be evaluated by numerical methods.

Trimer Model

In this model the trimer is considered as the dominant species at low concentration of alcohols [23,27]. Although the structure of trimer is not determined by IR spectroscopy, its presence can be confirmed by fitting IR data in this model. The mass balance equation in this model is:

$$C_a = C_1 + 3K_3C_1^3 \quad (13)$$

In this equation, K_3 is an unknown parameter which is to be determined.

LACT

Linear association with cyclic trimer (LACT) is also based on the presence of trimer [23,27]. In this model it is assumed that the species formed by hydrogen bonding is the cyclic trimer with the equilibrium constant K_3 and the species with higher mers have linear structure and have the same equilibrium constants K_{∞} . The mass balance equation is:

$$C_a = C_1 + 3K_3C_1^3 + 4K_3K_{\infty}C_1^4 + \dots + nK_3K_{\infty}^{n-3}C_1^n \quad (14)$$

which can be presented in the following simplified

form:

$$C_a = C_1 + \frac{K_3C_1^3(3-2K_{\infty}C_1)}{(1-K_{\infty}C_1)^2} \quad (15)$$

In the above equation, K_3 and K_{∞} are unknown which are to be determined by numerical methods.

DECM

In the dependent equilibrium constant model (DECM) [27] it is assumed that the probability of formation of different species in an associating mixture is not the same and depends on the size of n-mers. Considering the fact that on increasing the temperature the n-mers are decomposed to the lower-mers, such as trimer which are more stable at higher temperatures, the following equation, which shows an inverse functionality of $\ln K_n$ with association number n , is obtained

$$\ln K_n = \frac{D}{n-1} \quad (16)$$

where D is an unknown parameters, which should be determined.

Calculation of Excess Properties

For a binary mixture of alcohol (a) in solvent (s) the excess molar Gibbs free energy is expressed as:

$$g^E = RT(X_a \ln \gamma_a + X_s \ln \gamma_s) \quad (17)$$

where γ_a and γ_s are respectively activity coefficients of alcohol and solvent.

The excess enthalpy and entropy can be calculated using the following equations:

$$\frac{\partial(g^E/RT)}{\partial T} = -\frac{h^E}{RT^2} \quad (18)$$

$$s^E = \frac{h^E - g^E}{T} \quad (19)$$

According to lattice theory of Flory [24] the activity coefficients γ_a and γ_s can be expressed as [27]:

$$\ln \gamma_s = \ln \frac{\phi_s}{X_s} - \phi_a - \frac{\phi_a}{X_n} \cdot \frac{v_a}{v_s} + \frac{\beta}{RT} v_s \phi_a^2 \quad (20)$$

$$\ln \gamma_a = \ln \frac{\phi_a}{X_a \phi_{a1}^*} - \phi_s \frac{v_a}{v_s} + \frac{1}{X_n^*} - \frac{\phi_a}{X_n} + \frac{\beta}{RT} v_a \phi_s^2 \quad (21)$$

In the above equations the symbols have the following meanings; ϕ is volume fraction, X is mole fraction, v is molar volume, $\beta = (\delta_a - \delta_s)^2$, where δ is solubility parameter [31]. Also \bar{X}_n and \bar{X}_n^* are respectively the average number of segments per n-mers in solution and in pure alcohol. Hence, \bar{X}_n can be represented as:

$$\bar{X}_n = \frac{\phi_a}{\sum_{n=1}^{\infty} \frac{\phi_n}{n}} \quad (22)$$

To proceed with the excess function calculations we start with equation (22). ϕ_n is calculated by mass balance equation for each model using the values of equilibrium constant K_n obtained by curve fitting of spectroscopic results. Having \bar{X}_n the γ_a and γ_s are calculated by equations (20) and (21) and then are used in Eq. (17) to Eq. (19). It is worth noting that in the calculations the solubility parameters δ are obtained from reference [5].

Results and Discussion

The experimental data have been treated by the four models T, CLAM, LACT, DECM and based on the calculated correlation coefficient, the proper models for association of alcohol in each alcohol-solvent mixture compared with experimental results have been reported in Table 2 and Table 3. Table 2 shows that in the models in which the trimer is the dominant species, the calculated correlation coefficients are closer to unity. Therefore it can be stated that at low concentrations, the trimer is the dominant species in the alcohol-solvent mixtures. However, George *et al.* [33,34] by *ab initio* computations have shown that the tetramers are the most favored possible structure for molecular association of methanol and ethanol. Their results do not rule out our conclusion that the trimers are the most dominant species in the mixture, since experimental and the theoretical results indicate that various kinds of species such as monomer, dimer, cyclic trimer and cyclic tetramer are present in the mixture. Therefore it can be stated that while for the interactions between ethanol molecules (based on quantum mechanical

Table 2. Correlation coefficient values calculated for different models for alcohol+inert solvent mixtures

System	T (K)	Models			
		TRIMER	CLAM	LACT	DECM
Methanol+Hexane	298	0.99869	0.95058	0.98965	0.97301
Ethanol+Hexane	298	0.98161	0.97334	0.99798	0.98856
Cyclopentanol+Toluene	298	0.99958	0.99956	0.99934	0.99939
Ethanol+CCl ₄	313	0.99732	0.99273	0.99848	0.99198
Ethanol+CCl ₄	323	0.99163	0.99747	0.99966	0.99856
Ethanol+CCl ₄	333	0.99754	0.98951	0.99969	0.99865
Octanol+CCl ₄	298	0.99927	0.99851	0.99940	0.99913

Table 3. Equilibrium constants (K) for alcohol+inert solvent mixtures calculated by different models and the parameter D calculated for DECM model

System	T (K)	TRIMER	CLAM	LACT		DECM
		K3	K	K	K3	D
Methanol+Hexane	298	57.08	3.87	8.24	10.86	3.44
Ethanol+Hexane	298	55.88	3.76	8.41	11.89	3.45
Cyclopentanol+Toluene	298	0.58	0.28	1.31	0.999	0.97
Ethanol+CCl ₄	313	10.04	1.65	0.67	7.99	1.51
Ethanol+CCl ₄	323	5.73	1.22	0.978	3.75	1.11
Ethanol+CCl ₄	333	3.82	0.99	0.84	2.55	0.64
Octanol+CCl ₄	298	6.29	0.71	4.39	3.20	1.57

* Equilibrium constants are in terms of molar concentration unit.

energetic consideration) the tetramer is the most stable structure, for a mixture consisting various species the situation is quite different since the interactions among various species are involved and are not taken into account in quantum mechanical calculations.

On the other hand as it is seen in Table 2, for ethanol-carbon tetrachloride mixture with increasing temperature, the correlation coefficient gets closer to unity. This confirms the point that the trimer is the dominant species at higher temperature. Comparison of methanol and ethanol results in the Table 2 indicates that the probability of formation of trimer in methanol is much higher than that of ethanol. This is probably due to the higher polarity of methanol that increases the tendency towards more hydrogen bondings.

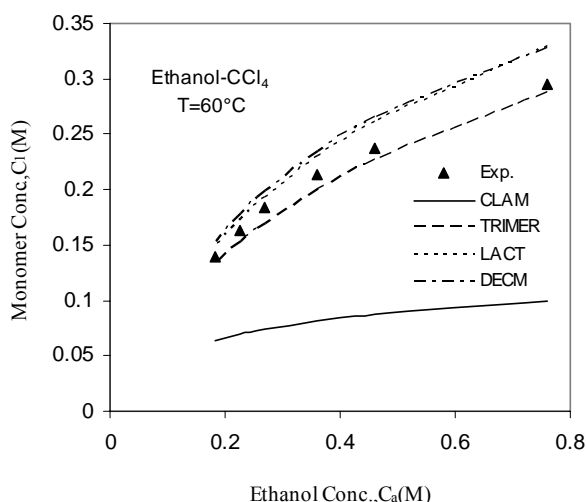


Figure 2. Calculated monomer concentration by different models versus alcohol concentrations in ethanol+CCl₄ mixture at 60°C.

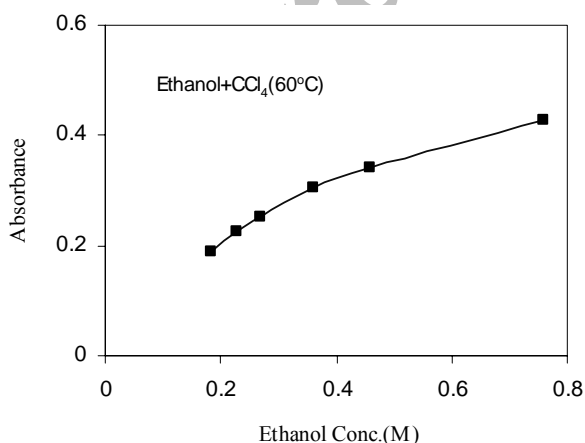


Figure 3. Variation of the measured absorbance versus ethanol concentration in ethanol+CCl₄ mixture at 60°C.

For ethanol-carbon tetrachloride at 60°C, as an example, the results of curve fitting of experimental results for concentration of monomer species by CLAM, T, LACT and DECM models are shown in Figure 2. As it is seen in this figure with increasing the number of hydrogen bondings and formation of multimers, the deviation of models from experimental results increases and this indicates the stability of trimer species in the mixture. Table 2 indicates that the calculated value of correlation coefficient for DECM model is close to that of LACT model. Therefore both models can be used for treating the experimental results.

Figure 3 is the plot of absorbances of free OH bonds versus concentration of ethanol in ethanol-carbon tetrachloride at 60°C. These plots show that with increasing the concentration of alcohol the absorbance of free monomer increases which is an indicator of increase in the net concentration of monomer. On the other hand Figure 4 shows that the distribution (relative concentration) of monomer decreases while the relative concentration of other species increases.

The value of enthalpy change on formation of trimer for ethanol in CCl₄ is -9.99 kcal/mol, when compared to that of multimer (-5 kcal/mol [32]) indicates the stability of trimer.

The calculated activity coefficients, excess Gibbs energy and excess enthalpy versus mole fraction of alcohols are given in Figures 5-7. The maximum at mole fraction 0.3-0.4 in Figures (6) and (7) are in agreement with those reported by other researchers [12,13].

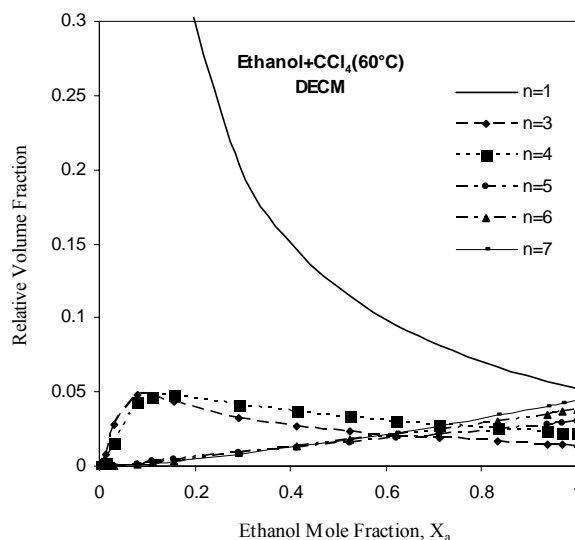


Figure 4. Calculated distributions (relative concentration) of species by DECM versus ethanol mole fraction in ethanol+CCl₄ mixture at 60°C.

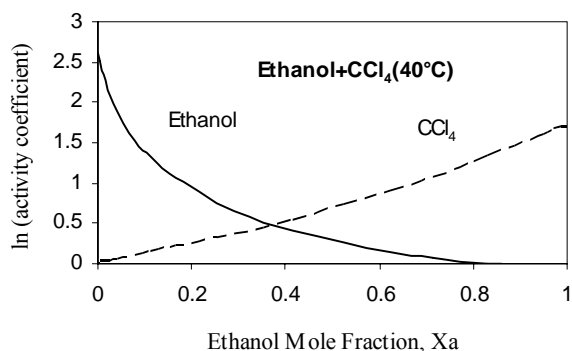


Figure 5. The calculated activity coefficients by LACT for ethanol and CCl_4 in ethanol+ CCl_4 mixtures at 40°C .

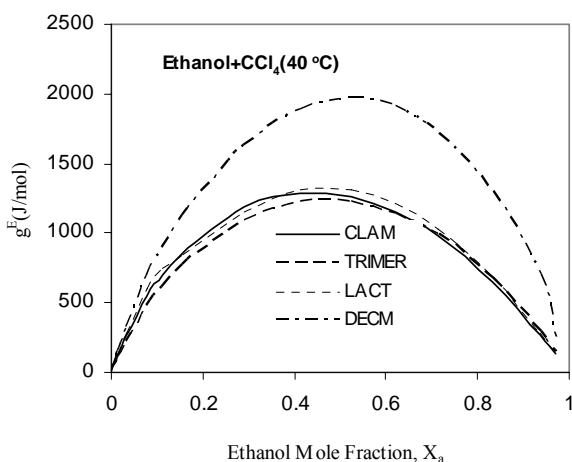


Figure 6. The calculated excess Gibbs function for ethanol+ CCl_4 mixture at 40°C using various association models.

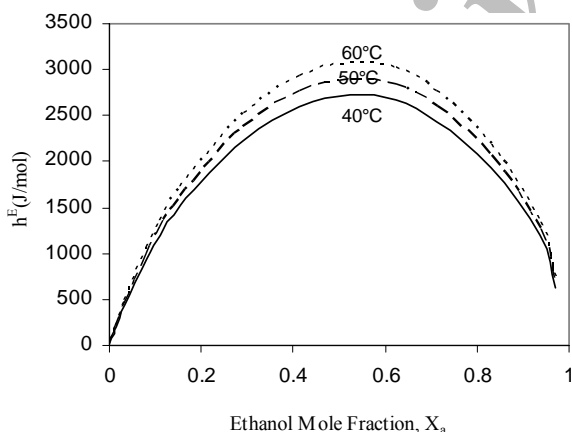


Figure 7. The calculated excess enthalpy for ethanol+ CCl_4 mixture at different temperatures using LACT model.

References

1. Pimentel G.C. and McClellan A.L. *The Hydrogen Bond*. Freeman, San Francisco (1960).
2. Hildebrand J.H. *J. Am. Chem. Soc.*, **51**: 66 (1929), and *J. Chem. Phys.*, **15**: 225 (1947).
3. Guggenheim E.A. *Mixtures*. Oxford, Oxford University Press (1952).
4. Wilson G.M., *J. Am. Chem. Soc.*, **86**: 127 (1964).
5. Prausnitz J.M., Lichtenthaler R.N., and de Azevedo E.G. *Molecular Thermodynamic of Fluid Phase Equilibria*, 3rd ed, New Jersey; Prentice Hall Inc. Press (1999).
6. Dolezalec F. *Z. Phys. Chem.*, **64**: 727 (1908).
7. Aghamiri S.F., Mansoori G.A., and Modarress H. *Ibid.*, **205**: 211 (1998).
8. Aghamiri S.F., Modarress H., and Mansoori G.A. *J. Phys. Chem. B*, **105**: 14 (2001).
9. Draye A.C., Tondeur J.J., and Vandendunghen G. *Spectrochimica Acta Part A*, **52**: 1757 (1996).
10. Xian-Da S., Wei-Qing L., Yun L., Jiane-He X., and Yao-Hui C. *Thermochimica Acta*, **176**: 305 (1991).
11. Schwager F., Marand E., and Davis R.M. *J. Phys. Chem.*, **100**: 19268 (1996).
12. Martinez S. *Spectrochimica Acta Part A* 46, **9**: 1395 (1990).
13. Martinez S., *Spectrochimica Acta Part A* 42, **4**: 511 (1986).
14. Griffiths V.S. and Socrates G. *J. Mol. Spect.*, **21**: 302 (1966).
15. Kunst M., Van Duijn D., and Bordewijk P. *Ber. Bunsengen, Phys. Chem.*, **83**: 840 (1979).
16. Brink G. and Glasser L. *J. Phys. Chem.*, **82**(9): 1000 (1978).
17. Robinson S.Ch. *J. Chem. Eng. Part*, **22**: 319 (1966).
18. Damewood J.R.Jr. and Kumpf C.F. *J. Phys. Chem.*, **94**: 6619 (1990).
19. Nodland E. *Chemomet. Int. Lab. Systems*, **49**: 33 (1999).
20. Nodland E. *Appl. Spect.*, **54**(9): 1399 (2000).
21. Vingaradov S.N. and Linnell R.H. *Hydrogen Bonding: Van Nostrand Reinhold Co*, New York (1971).
22. Luck W.A.P. and Schrems O. *J. Mol. Struct.*, **60**: 333 (1980).
23. Tucker Edwin E. and Becker Edwin D. *J. Phys. Chem.*, **77**(14): 1783 (1973).
24. Flory P.J. *Principles of Polymer Chemistry*. Cornell University Press, Ithace, and New York, P. 495 (1953), and *J. Chem. Phys.*, **12**: 25 (1944).
25. Storek W. and Kriegsman H., *Ber. Bunsenges. Phys. Chem.*, **72**: 706 (1968).
26. Coggeshall N.D. and Saier E.L. *J. Am. Chem. Soc.*, **73**: 5314 (1951).
27. Karachewski A.M. and Eckert C.A. *AIChE.*, **28**: 315 (1991).
28. Kretschmer C.B. and Wiebe R.J. *J. Chem. Phys.*, **22**: 1697 (1954).
29. Renon H., Prausnitz J.M., and Scott R.L. *Regular and Related Solution*. Van Nostrand Reinhold Co., New York, P. 126 (1970).
30. Duboc C. *Spectrochim. Acta part A*, **30**: 431 (1974).
31. Scatchard G. *Chem. Rev.*, **2**: 425 (1949).
32. Coleman M.M., Graf J.F., and Painter P.C. *Specific Interactions and the Miscibility of Polymers Blends*. Technomic, Lancaster (1991).
33. George W.O., Has T., Hossain Md.F., Jones B.F., Lewis R., and Price J.M. *J. Chem. Soc., Faraday Trans.*, **18**: 2701 (1998).
34. Dixon J.R., George W.O., Hossain Md.F., Lewis R., and Price J.M. *Ibid.*, **20**: 3611 (1997).