

Correlation of ^1H NMR Chemical Shift for Alcohol + Inert Solvent Mixtures by LFHB Model*

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Abstract The lattice-fluid hydrogen bond equation of state model(LFHB model) is used to correlate ^1H NMR chemical shift of the proton in hydroxyl(—OH) of alcohol + inert solvent mixtures. The 29 sets of data for 17 systems are correlated using only one parameter. In addition, this parameter can be used to predict the chemical shift of mixtures at different temperatures.

Keywords: ^1H NMR chemical shift, Hydrogen bond, Lattice fluid theory, Alcohol

The relationship between spectroscopic data and statistical thermodynamic theory interested many researchers. In 1953, Gutowsky *et al.*^[1] proposed a relationship between them. One attestation for the theories is the ability to correlate and predict spectroscopic data. Several approaches were proposed. The chemical association theory^[2-4] is the most commonly used which regards the equilibrium among all assumed complexes. The local model in which physical and chemical effects are mixed is regarded more as a physical model. There is still a third approach proposed by Levine, Perram^[5] and Luck^[6], which focuses only on the formation and rupture of hydrogen bonds for modeling complex systems. Both SAFT^[7-10] and LFHB EOS^[11] are based on such assumption for hydrogen bonds in liquids, though their thermodynamical treatment differs.

As previous work of our group, ^1H NMR chemical shifts of DMF+H₂O^[12], NMA +CCl₄ and NMA+H₂O^[13] were correlated by chemical association theory. Deng *et al.*^[14] for the first time used a simple local composition model to correlate the chemical shifts of mixtures and successfully simultaneously correlated viscosity and ^1H NMR chemical shift for DMF-methanol systems^[15]. The local composition model is also used to predict vapor-liquid equilibrium^[16] and viscosity^[17]. The SAFT theory has also been applied to such studies on spectroscopy and satisfactory results achieved^[18]. A detailed comparison of SAFT and Wilson local composition model was also given^[19]. As a comparison and supplement we introduced LFHB EOS into our study and compare it with the popular chemical association theory. With the one

correlated parameter and parameters of the LFHB EOS, we also try to predict the ^1H NMR chemical shift of the mixture at different temperatures.

1 Theory

Gutowsky *et al.*^[11] presented such an assumption that the measured chemical shift is a weight-average of all species shifts due to the fact that the lifetime of a hydrogen bond is much shorter than the NMR observation time. We assume that the observed chemical shifts of the hydroxyl proton are due to two species, i. e., hydrogen bond OH proton and non-bonded OH. Then the observed chemical shift is expressed as

$$\delta_{\text{obs}} = x_f \delta_f + x_{\text{hb}} \delta_{\text{hb}} - (1 - x_{\text{hb}}) \delta_f + x_{\text{hb}} \delta_{\text{hb}} \quad (1)$$

Where x_f and δ_f are molar fraction and chemical shift for non-bonded OH. x_{hb} and δ_{hb} are molar fraction and chemical shift for hydrogen bond OH. x_{hb} is also called the hydrogen bond extent. For pure alkanols,

$$x_{\text{hb}}^0 = \frac{\delta_{\text{obs}}^0 - \delta_f}{\delta_{\text{hb}} - \delta_f} \quad (2)$$

Where superscript 0 denotes pure material. Rewrite the above equation, we can get

$$\delta_{\text{obs}} = \frac{x_{\text{hb}}}{x_{\text{hb}}^0} (\delta_{\text{obs}}^0 - \delta_f) + \delta_f \quad (3)$$

If we can calculate the hydrogen bond extent (x_{hb}) in pure and mixed systems, only δ_f remains unknown in equation (3). Thus we can get δ_f by correlating experimental chemical shifts of mixtures. In this paper, we try to use the LFHB model on chemical shifts correlation. Firstly we will see how to get the hydrogen

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bond extent, which is to be used in correlating NMR chemical shifts, from the LFHB theory.

Invoking arguments originally proposed by Levine and Perram^[5], Veytsman theorized that the properties of a hydrogen bond fluid depended on the number of arrangements of hydrogen bonds in the system but not on the distribution of the associates^[20]. Recently, Panayiotou and Sanchez^[11] made a significant step in this direction by incorporating the Perram-Veytsman theory of hydrogen bond into the original Sanchez-Lacombe equation of state^[21]. It can successfully calculate some thermodynamic properties such as H^E and V^E ^[22]. Compared with Luck's IR data^[6] of pure alcohols, the hydrogen bond extent in this theory shows the perfect physical meaning. However the IR data for mixtures are scarce and the whole concentration data are hard to get. Hence when it comes to investigate the hydrogen bond in whole concentration of the mixtures, the NMR chemical shift is a good attestation^[2]. It verifies that by incorporating the Perram-Veytsman theory in the context of the Sanchez-Lacombe equation of state, the LFHB yields considerable accuracy in the representation of spectroscopy data besides phase equilibrium in hydrogen bond fluids.

In LFHB theory, the partition function Q is divided into chemical and physical terms,

$$Q = Q_p Q_H \quad (4)$$

Where Q_p and Q_H are physical and chemical terms, respectively.

The physical partition function is taken from the original Scanchz-Lacombe lattice fluid EOS^[21]. We can get the chemical term by counting how the hydrogen bonds are distributed in the lattice fluids by statistical theory,

$$Q_H = \left(\frac{\tilde{p}}{rN} \right)^{N_H} \Omega \exp \left(- \frac{\sum N_{ij} G_{ij}^0}{kT} \right) \quad (5)$$

Where \tilde{p} is the reduced density, r is the number of segments per molecule. N is the total number of molecules in the system. N_{ij} is the number of hydrogen bond formed by proton donor i and acceptor j in the system characterized by a free energy G_{ij}^0 and $N_H = \sum N_{ij}$ is the total number of intermolecular hydrogen bonds. The preexponential factor Ω is the number of different ways of distributing the hydrogen bonds in the system. Then if there is only one kind of donor (presented in N_{11} as the first subscript 1) and acceptor (presented in N_{11} as the second subscript 1), thus only one kind of hydrogen bond can be formed in the system such as in alcohols, we have

$$\Omega = \frac{N!}{(N-N_{11})! N_{11}! (N-N_{11})! N_{11}!} \quad (6)$$

$$G_{11}^0 = E_{11}^0 + pV_{11}^0 - TS_{11}^0 \quad (7)$$

Where $E_{11}^0 = -25.1 \text{ kJ} \cdot \text{mol}^{-1}$, $S_{11}^0 = -26.5 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, $V_{11}^0 = -5.6 \text{ cm}^3 \cdot \text{mol}^{-1}$. Also the first subscript 1 stands for the kind of donor,

the second subscript 1 stands for the kind of acceptor, and N_{11} stands for the number of hydrogen bonds formed in the system. In this model, the energy E_{11}^0 , entropy S_{11}^0 and volume V_{11}^0 of for formation of a hydrogen bond are assumed to be constants and identical to all 1-alkanols. The temperature influence on hydrogen bond is included in the G_{11}^0 , as in Equation (7). They are comparable to the widely used values in various association models and can be used successfully to predict a microscopic property, the degree of hydrogen bond at different temperatures^[23]. This selection of such values is, to some extent, arbitrary, and possibly other sets of values would reproduce experimental data more quantitatively^[22]. Thus the chemical Gibbs free energy can be derived,

$$\frac{G_H}{RT} = \gamma N \left\{ \sum_i^m \sum_j^n v_{ij} \left[1 + \frac{G_{ij}^0}{RT} + \ln \frac{\tilde{v} v_{ij}}{v_{i0} v_{j0}} \right] + \sum_i^m v_d^i \ln \frac{v_{d0}}{v_d^i} + \sum_j^n v_a^j \ln \frac{v_{a0}}{v_a^j} \right\} \quad (8)$$

Where $v_{ij} = \frac{N_{ij}}{rN} = \frac{(x_{ib})_{ij}}{r}$, $v_d^i = \frac{N_d^i}{rN}$. The physical free Gibbs energy of the system is just as that of the original S-L EOS^[21],

$$\frac{G_p}{k_B T} = rN \left\{ - \frac{\tilde{p}}{\tilde{T}} + \frac{\tilde{p}\tilde{v}}{\tilde{T}} + (\tilde{v}-1) \ln(1-\tilde{\rho}) + \frac{1}{r} \ln \tilde{\rho} + \sum_{i=1}^i \frac{\phi_i}{r_i} \ln \frac{\phi_i}{\omega_i} \right\} \quad (9)$$

Where ϕ_i and ω_i are the segment fraction and the number of configurations available to an r_i -mer in the closed-paced pure state. Thus we can get the hydrogen bond lattice fluid EOS,

$$\tilde{\rho}^2 + \tilde{p} + \tilde{T} \left[\ln(1-\tilde{\rho}) + \tilde{\rho} \left(1 - \frac{1}{\tilde{r}} \right) \right] = 0 \quad (10)$$

Where \tilde{p} , \tilde{T} and \tilde{v} are the reduced pressure, temperature and volume, respectively. At the same time we can get the expression for v_{11} , or we can write it as $x_{ib} = r v_{11}$,

$$\frac{v_{11}}{v_{10} \omega_{01}} = \exp \left(- \frac{G_{11}^0}{RT} \right) \quad (11)$$

Pure parameters listed in Table 1 are optimized for saturated liquid densities and vapor pressures.

If the pure parameters are used in the equation of state (EOS), we can extract the hydrogen bond extent of the pure system, x_{ib}^0 . If the mixed parameters under different concentrations are used, we can get the hydrogen bond extent of the mixed system, x_{ib} . With the calculated x_{ib}^0 for pure alkanol and x_{ib} for mix-

Table 1 Pure parameters^[11]

Compound	T^*/K	ρ^*/MPa	$\rho^*/kg \cdot m^{-3}$
hexane	476	298	775
CCl ₄	535	381	1790
heptane	487	309	800
cyclohexane	497	383	902
methanol	496	315	786
ethanol	464	328	826
1-propanol	478	320	858
1-butanol	494	320	863
1-pentanol	513	313	865
1-hexanol	534	301	867
octanol	552	301	872

* denotes the parameter for pure compound.

tures at different concentrations from LFHB, we can now fit the ^1H NMR experimental data to get the only one optimum δ_f in equation (3), with the following objective function,

$$J = \sqrt{\frac{1}{(n-1)} \sum_{i=1}^n (\delta_{\text{cal}} - \delta_{\text{obs}})^2} \quad (12)$$

The δ_{hb} can also be obtained from above calculation. Correlation results are listed in Table 2, where $\Delta\delta$ and $\Delta\delta\%$ stand for the absolute and relative correlation root-mean square deviation (RMSD), respectively. The correlation result shows good physical meaning for δ_f .

Furthermore, the chemical shift of non-hydrogen bond proton is usually considered as a constant at common range of temperature. Therefore using δ_f at one common temperature we can predict chemical shifts of binary system at other temperatures. The butanol + cyclohexane system is taken as an example for prediction as showed in Fig. 1. The δ_f correlated at 326.2 K is used as a known parameter to predict chemical shifts at 307.2 K and 347.2 K, respectively. The RMSD of prediction are 4.68% and 2.72%, respectively, which is a little higher than those of correlation.

2 Results and Discussion

In this paper the hydrogen bond lattice fluid theory is used to correlate the chemical shift of the alcohol + inert solvent mix-

Table 2 Correlated results for alcohol + inert solvent

System	T/K	δ_f	$\Delta\delta$	$\Delta\delta\%$	Reference
methanol+hexane	298.2	-0.59	0.24	6.65	[24]
methanol+hexane	308.2	0.19	0.30	9.00	[24]
methanol+hexane	318.2	0.17	0.17	4.72	[24]
methanol+hexane	328.2	2.30	0.18	4.43	[24]
methanol+cyclohexane	324.2	196.93 Hz	15.20 Hz	1.96	[3]
methanol+cyclohexane	331.2	128.82 Hz	20.69 Hz	2.84	[3]
methanol+cyclohexane	337.2	76.08 Hz	22.66 Hz	3.32	[3]
methanol+heptane	328.2	-117.70 Hz	23.12 Hz	2.66	[3]
methanol+heptane	333.2	-186.69 Hz	26.15 Hz	3.08	[3]
methanol+heptane	337.2	-225.19 Hz	29.59 Hz	3.56	[3]
methanol+CCl ₄	298.2	0.39	0.14	4.33	[25]
methanol+CCl ₄	313.2	-4.61	0.03	1.08	[26]
ethanol+hexane	298.2	0.53	0.15	4.06	[2]
ethanol+cyclohexane	296.2	1.03	0.17	4.61	[2]
ethanol+cyclohexane	298.2	0.66	0.23	7.18	[27]
1-propanol+hexane	296.2	-0.12	0.10	2.35	[2]
1-propanol+cyclohexane	296.2	0.97	0.06	1.50	[2]
1-propanol+CCl ₄	308.2	-153.91 Hz	4.02 Hz	1.21	[28]
1-butanol+hexane	296.2	-0.31	0.08	2.19	[2]
1-butanol+cyclohexane	296.2	0.59	0.08	2.29	[2]
1-butanol+cyclohexane	307.2	30.23 Hz	26.1 Hz	3.87	[2]
1-butanol+cyclohexane	326.2	38.74 Hz	17.6 Hz	1.82	[2]
1-butanol+cyclohexane	347.2	38.62 Hz	15.1 Hz	1.62	[3]
pentanol+hexane	296.2	-0.35	0.06	1.56	[2]
pentanol+cyclohexane	296.2	0.83	0.05	1.34	[2]
hexanol+hexane	296.2	-0.48	0.07	2.13	[2]
hexanol+cyclohexane	296.2	0.75	0.07	2.33	[2]
octanol+hexane	296.2	-1.06	0.06	1.62	[2]
octanol+cyclohexane	296.2	0.56	0.04	1.11	[2]

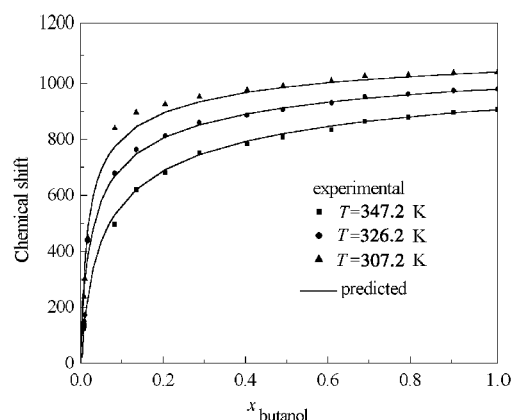


Fig. 1 Predicted and experimental chemical shifts of butanol + cyclohexane

tures. Parameters for pure components are listed in Table 1^[11]. All correlation results are listed in Table 2. For comparison we carried out another correlation by equation (9) using 2 parameters: δ_{hb} and δ_f , which stand for the characteristic chemical shift of hydrogen bond OH proton and non-bonded OH, respectively. Almost the same results including the parameters are obtained. The optimized value of δ_f is found to be physically meaningful for characteristic chemical shift of non-hydrogen bond OH. This attested the validity of correlation using only one parameter. With the gotten parameter δ_f , the ^1H NMR at different temperatures can be predicted.

Results are compared with chemical association theory. In comparison with longer alcohols, the correlation is not so satisfactory for methanol. The hydrogen bond extent in the mixture calculated from LFHB and that from correlating the ^1H NMR by chemical association theory can be seen in Fig. 2.

The hydrogen bond extent in methanol + hexane calculated by LFHB is lower than that by the chemical association theory, especially at dilute concentrations for x_{methanol} around 0.1. While hydrogen bond extents from both theories agree very well in whole concentration range for butanol + cyclohexane. Therefore

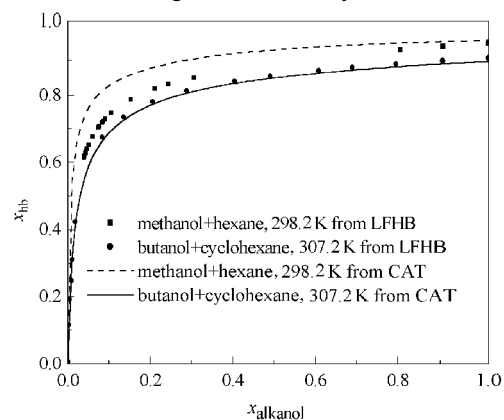


Fig. 2 Comparison for the calculated hydrogen bond extents from LFHB and chemical association theory (CAT)

the difference explains why the correlation results for methanol + hexane system in Table 1 are not so good. It may be caused by the strong cooperative effect in methanol at dilute concentration. Thus it shows the cooperative effects will be very important for some alcohols mixtures.

Such results may also be due to the foreordination of accepted chemical parameters for hydrogen bond. We found hydrogen bond extents are more affected by the hydrogen bond parameters under certain pressure. For pressure at 101.325 kPa, we give a tiny perturbation to chemical or physical parameters. It is found that calculated hydrogen bond extents are more affected by the chemical parameters and calculated densities are more related to the physical ones. Thus it needs more detailed study on the parameters and how to get the chemical parameters for hydrogen bond.

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基于 LFHB 理论模型关联和预测醇+惰性溶剂的 ^1H NMR 化学位移*

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摘要 运用含氢键缔合的格子流体状态方程(LFHB), 仅用一个参数关联了一元醇-惰性溶剂共 17 个体系 29 套 ^1H NMR 化学位移数据. 并且用关联参数成功预测了不同温度下丁醇+环己烷的化学位移. 所得结果与化学缔合理论的结果进行了比较. 对于某些体系在稀浓度范围 LFHB 的计算氢键缔合度要低于化学缔合理论的结果. 并且分析了 LFHB 理论中的物理参数和化学参数对于缔合度计算的不同影响.

关键词: ^1H NMR 化学位移, 氢键, 格子流体理论, 醇

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