Simultaneous Correlation of Viscosity and ¹H NMR Chemical Shift Data for DMF-methanol System*

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Abstract　　A new model based on the concept of local composition has been proposed for the correlation of the NMR chemical shift data. Consequently, the viscosity and NMR chemical shift data were well correlated simultaneously using this model and the early proposed local composition viscosity equation. The resulting average absolute deviations of viscosity and NMR chemical shift are respectively less than 0.0006 mPa・s and 0.0072, which suggested the reasonability of the proposed model.

Keywords:　　NMR,　　Viscosity,　　Chemical shift,　　Correlation,　　Spectroscopy

Viscosity and ¹H NMR chemical shift belong traditionally to two different kinds of properties, i. e. transport and spectroscopy properties. Viscosity is an important property to be considered in process of product design and optimization. For pure liquid and liquid mixture viscosity prediction, either the Eyring′s absolute rate theory [1] or free volume theory for fluidity [2] has been used. A series [3-5] of equations have been developed on the basis of the Eyring′s theory for viscosity correlation. Another application [6-8] of Eyring′s theory is combining models for viscosity calculation with the local composition concept. Cao [9-10] developed a statistical thermodynamic model. Also some group-contribution models have been presented [11-12].

Spectroscopic techniques have been extensively used to investigate the solution structure and provide physically meaningful information on intermolecular interactions. In particular, NMR allows one to probe associated mixture behavior on the molecular level and has become increasingly popular in recent years [13]. For the correlation between the ¹H NMR chemical shift and composition of hydrogen-bonding mixtures,

several association models [14-17] have been proposed on Gutowsky and Saika′s assumption [18]. Although chemical association models give a direct understanding for the change of the chemical shifts, the primary disadvantage is the large number of adjustable parameters, which must be obtained especially for systems exhibiting a large degree of association.

In the previous works, thermodynamic information（e. g., vapor-liquid equilibrium（VLE）data）and viscosity of liquid mixtures have been simultaneously correlated or predicted [9-10]. In this paper, a new local composition model is developed, from which both viscosity and ¹H NMR shift can be expressed by the same energy parameters. This feature makes it possible to correlate the viscosity and ¹H NMR chemical shift values simultaneously for the associated binary system.

1　Models for ¹H NMR chemical shift and viscosity

The chemical shifts of associated mixture are very complicated, which include the contributions from the local magnetic field, the magnetizability

anisotropy, electrostatic polarization and electronic structure. To simplify, we assume that the observed ^{1}H NMR chemical shift at a certain composition can be expressed as following,

$$\delta_i = \delta_i^0 \varphi_{ii} + \delta_i^\infty \varphi_{ij} \tag{1}$$

where φ_{ii}, φ_{ij} are local volume fractions of molecule i and j around central molecule i, respectively. δ_i^0, δ_i^∞ are chemical shift of molecule i for pure substance and infinite dilute chemical shift of molecule i, respectively, which are defined as following: for any component molecule i ($i = 1$ or 2) in a binary solution, when i is surrounded by itself molecule completely, the measured chemical shift is defined as pure substance chemical shift. In turn, when i is surrounded by the other molecule completely, the measured chemical shift is defined as infinite dilute chemical shift, usually obtained by extrapolating the dilute chemical shifts to zero concentration.

According to the concept of local composition[19], for a binary solution of components i and j, the probability of finding a molecule of type j compared to that of finding a molecule of type i about the central molecule of type i is given by,

$$\frac{x_{ij}}{x_{ii}} = \frac{x_j \exp\left(-\lambda_{ij}/RT\right)}{x_i \exp\left(-\lambda_{ii}/RT\right)} \tag{2}$$

The above equation demonstrates that the ratio of the amounts of j and i molecules around a central i molecule is equal to the ratio of the mole fraction of j and i weighted statistically by the Boltzmann factors $\exp(-\lambda_{ij}/RT)$ and $\exp(-\lambda_{ii}/RT)$. λ_{ij} and λ_{ii} are, respectively, proportional to the i-j and i-i interaction energies.

As the molecule of type i is concerned, the local compositions sum to unity,

$$x_{ii} + x_{ij} = 1 \tag{3}$$

We redefine local volume fractions as:

$$\varphi_{ii} = \frac{x_{ii}V_i}{x_{ii}V_i + x_{ij}V_j} \tag{4}$$

$$\varphi_{ij} = \frac{x_{ij}V_j}{x_{ii}V_i + x_{ij}V_j} \tag{5}$$

If we define:

$$\Lambda_{ij} = \frac{V_j}{V_i}\exp\left[-\left(\lambda_{ij} - \lambda_{ii}\right)/RT\right] \tag{6}$$

then, by combination of equation $(2) \sim (6)$, the local mole volume fractions can be simplified as,

$$\varphi_{ii} = \frac{x_i}{x_i + \Lambda_{ij}x_j} \tag{7}$$

$$\varphi_{ij} = \frac{\Lambda_{ij}x_j}{x_i + \Lambda_{ij}x_j} \tag{8}$$

For correlation of viscosity (η) of polar binary system ($i = 1$ and 2), a reported equation[9-10] is used as following,

$$\ln\left(\eta V\right) = \sum_{i=1}^{2} \phi_i\ln\left(\eta_i V_i\right) + 2\sum_{i=1}^{2} \phi_i\ln\left(x_i/\phi_i\right) - \\ \sum_{i=1}^{2}\left(q_i n_i \phi_i/r_i\right)\sum_{j=1}^{2}\theta_{ji}\ln\left(\tau_{ji}\right) \tag{9}$$

$$V = \sum x_i V_i \quad \phi_i = x_i r_i / \sum_{j=1}^{2} x_j r_j \quad \theta_i = x_i q_i / \sum_{j=1}^{2} x_j q_j$$

$$\theta_{ji} = \theta_j \tau_{ji} / \sum_{j=1}^{2} \theta_j \tau_{ji} \quad \tau_{ji} = \exp\left(-\frac{\lambda_{ji} - \lambda_{ii}}{RT}\right) \tag{10}$$

where η_i and V_i denote the viscosity and molar volume. r_i and q_i are group volume and surface area calculated by UNIFAC method[20]. n_i, the proportional constant, is set to be 2.0 according to the literature[10].

In the above equations, $\lambda_{ij} = \lambda_{ji}$. So, $\lambda_{ij} - \lambda_{ii}$ were used as the mutual parameters for simultaneous correlation of viscosity and ^{1}H NMR chemical shift data.

2　Experimental section
2.1　Materials

Methanol and *N, N*-dimethylformamide（DMF）of analytical-reagent grade（Shanghai chemical reagent Co.）were purified according to the literature[21]. The mass fraction of each solvent, as checked by gas chromatograph, was better than 99.95%.

2.2　Sample preparation

All the samples covering the whole composition range were prepared by weighing pure components. A small volume（$\varphi_v = 0.001$, φ_v is volume fraction）of tetramethylsilane（TMS）was added to the pure solvents from which the samples were prepared.

2.3　Instrumentation

A Bruker advance DMX spectrometer was used

Table 1　　The experimental and calculated ¹H NMR chemical shift for methanol (1) + DMF (2) at 298.1 K

x_1	δ-OH (exp)	δ-OH(cal)	δ-CHO(exp)	δ-CHO (cal)
0.0000	4.0647[a]	4.0647	8.0276	8.0276
0.0071	4.0677	4.0680	8.0270	8.0274
0.0148	4.0694	4.0717	8.0267	8.0271
0.1034	4.1013	4.1156	8.0243	8.0244
0.2561	4.1808	4.2006	8.0195	8.0191
0.4383	4.3026	4.3211	8.0127	8.0116
0.6008	4.4405	4.4513	8.0034	8.0035
0.7579	4.6066	4.6048	7.9923	7.9938
0.9523	4.8567	4.8475	7.9796	7.9784
0.9919	4.9110	4.9063	7.9753	7.9746
0.9964	4.9155	4.9132	7.9744	7.9742
0.9973	4.9176	4.9147	7.9744	7.9741
1.0000	4.9188	4.9188	7.9738[b]	7.9738

δ-OH: the ¹H NMR chemical shifts of methanol hydroxyl proton, δ-CHO: the ¹HNMR chemical shifts of DMF carboxyl group proton.

a)obtained by extrapolating of given δ-OH to methanol infinite dilution, b)obtained by extrapolating of given δ-CHO to DMF infinite dilution

to measure the chemical shifts of each sample, the working frequency being 500.13 MHz. The uncertainty of the measurement of the chemical shift was 0.38 Hz. The temperature was stable to within (298.1 ± 0.1) K.

3　　Results and discussion

It is not difficult to fit the ¹H NMR shift and viscosity data separately. However, the resulting parameters, which should be theoretically treated as identical, will not be the same in fact. The actual goal is always to improve understanding of molecular interactions by using an integrated approach to data analysis. For the above reasons, we focus on the simultaneous fitting of ¹H NMR shift and viscosity data. The modified Powell method[22] was used to minimize the following objective function, which is the linear summation of root-mean square deviations for chemical shifts and viscosity.

$$O.F. = \left[\frac{1}{l-1}\sum_{i=1}^{l}\left(\frac{\delta_{i,CHO}^{cal}-\delta_{i,CHO}^{exp}}{\delta_{i,CHO}^{exp}}\right)^2\right]^{1/2} +$$
$$\left[\frac{1}{m-1}\sum_{i=1}^{m}\left(\frac{\delta_{i,OH}^{cal}-\delta_{i,OH}^{exp}}{\delta_{i,OH}^{exp}}\right)^2\right]^{1/2} +$$
$$\left[\frac{1}{n-1}\sum_{i=1}^{n}\left(\frac{\eta_i^{cal}-\eta_i^{exp}}{\eta_i^{exp}}\right)^2\right]^{1/2} \quad (11)$$

where l, m, n are the numbers of carboxyl group proton, hydroxyl proton chemical shift and viscosity data points, respectively. $\delta_{i,CHO}^{cal}$ and $\delta_{i,OH}^{cal}$, are calculated chemical shift of carboxyl group pro-

ton, hydroxyl proton according to equation(1), respectively. η_i^{exp} is the calculated viscosity according to the equation(9). $\delta_{i,CHO}^{exp}$, $\delta_{i,OH}^{exp}$ and η_i^{exp} are experimental values.

The energy parameters, $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{21} - \lambda_{22})$, are equal to 106.98 J·mol⁻¹ and −46.52 J·mol⁻¹ by minimizing the above object function. In turn, the calculated chemical shift and viscosity values are obtained by using the above energy parameters and corresponding equations(1), (9). Table 1 includes experimental and calculated ¹H NMR shift values of methanol hydroxyl and DMF carboxyl group proton of methanol + DMF at 298.1 K. Table 2 lists the experimental[23] and calculated viscosity for the same system.

The AAD(average absolute deviation) and RMSD(root-mean square deviation) are given by,

$$AAD = \frac{1}{m}\sum_{1}^{m}|Q_{cal} - Q_{exp}| \quad (12)$$

Table 2　　The experimental and calculated viscosity for methanol (1) + DMF (2) at 298.15 K

x_1	η(exp)/mPa·s	η(cal)/mPa·s
0.0000	0.7960	0.7960
0.1198	0.7660	0.7655
0.2267	0.7390	0.7384
0.4094	0.6930	0.6922
0.5596	0.6550	0.6546
0.6854	0.6230	0.6230
0.7922	0.5960	0.5964
0.8840	0.5730	0.5737
0.9639	0.5530	0.5539
1.0000	0.5450	0.5450

$$RMSD = \left(\frac{1}{m-1} \sum_{1}^{m} \left(\frac{Q_{exp} - Q_{cal}}{Q_{exp}} \right)^2 \right)^{1/2} \quad (13)$$

where Q denotes the ^{1}H NMR chemical shift(δ) or viscosity(η) in the paper, m is the number of data points. The AAD of hydroxyl and carboxyl group proton shift are 0.0072 and 0.0005, respectively. The RMSD of hydroxyl and carboxyl group proton shift are 0.00242 and 0.000093 respectively. The AAD and RMSD of viscosity are 0.0006 and 0.00104 mPa·s, respectively. It is known that the proposed local composition model can give good ^{1}H NMR chemical shift description. The spectroscopy and transport properties can be simultaneously correlated successfully.

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DMF- 甲醇体系粘度与核磁共振化学位移的同时关联 *

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摘要   提出了一个基于局部组成概念上的核磁共振模型. 利用该模型和以前别人提出的局部组成型粘度方程, 成功地同时关联属于传递性质的粘度数据和属于波谱性质的核磁共振化学位移数据, 关联所得到化学位移的平均绝对偏差小于 0.0072, 粘度的平均绝对偏差小于 0.0006 mPa·s, 结果表明提出的局部组成模型是合理的.

关键词: 核磁共振,   粘度,   化学位移,   关联,   波谱

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