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Prediction of vapor–liquid equilibria of alcohol + hydrocarbon systems by ^{1}H NMR spectroscopy

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ABSTRACT

The ^{1}H NMR chemical shifts of alcohol + hydrocarbon systems over the whole concentration range at 298.15 K were measured. Based on the concept of local composition (LC), the concentration-dependent ^{1}H NMR chemical shift data of the OH and CH groups for 13 alcohol + hydrocarbon systems were correlated with only one energy parameter, respectively. Using the parameters obtained from the spectra alone, the isothermal and isobaric vapor–liquid equilibria (VLE) data of the above-mentioned alcohol + hydrocarbon systems were predicted with satisfactory results. By this way, the spectroscopic information can be used to predict VLE data of alcohol + hydrocarbon systems directly.

1. Introduction

Vapor–liquid equilibria (VLE) data are essential for the development and design of separation sequences of mixtures in the chemical, petrochemical, and pharmaceutical industries. For example, in the analysis of distillation and other vapor–liquid separation processes, one must estimate the compositions of the vapor and liquid mixtures in the equilibrium. So far, a great deal of VLE data for different systems have been measured and accumulated, and the measurement of VLE is still continuing. Moreover, many equations are developed to correlate VLE data of binary and multi-component mixtures based on the Wilson's local composition concept (Wilson, 1964), such as Wilson equation (Orye and Prausnitz, 1965), NRTL equation (Renon and Prausnitz, 1968), UNIQUAC equation (Abrams and Prausnitz, 1975; Maurer and Prausnitz, 1978), etc. By correlating the VLE data of mixtures, the corresponding adjustable parameters could be obtained.

Simple prediction methods rather than direct measurement approaches are of great importance to estimate the required VLE data, which are difficult to measure, or the measurement is not economical. In the past years there has been a rapid growth in the reports on the prediction of VLE data. For example, the infinite dilution activity coefficient model is a traditional method, which is used two activity coefficients at infinite dilution of binary mixtures and coupled with local composition equation at infinite dilution to predict the VLE (Schreibe and Eckert, 1971; Nicolaides and Eckert, 1978; Eckert et al., 1981; Loblen and Prausnitz, 1982). However, for most highly nonideal binary systems, it is very difficult to obtain both two activity coefficients at infinite dilution simultaneously because the activity coefficient at infinite dilution of the steady component is difficult to directly measure. Besides the infinite dilution activity coefficient model, some thermodynamic models combining with the equation of state are also used to predict the VLE of the symmetric systems and asymmetric systems (Weidlich and Gmehling, 1987; Holderbaum and Gmehling, 1991; Gmehling et al., 1993; Liu and Hu, 1998; Ghosh and Taraphdar, 1998; Ahlers and Gmehling, 2002; Voutsas et al., 2006; Haghtalab and Mahmoodi, 2010; Fan et al., 2011). But this method is sometimes limited by choosing appropriate mixing rule and certain assumptions to reduce the number of adjustable parameters. Therefore, it is necessary to develop another method to estimate VLE data of mixtures.

In recent years, spectroscopic techniques have been extensively used to study the thermodynamic properties and hydrogen bonding interactions of associated systems (Johnston et al., 1996; Mizuno et al., 1997; Gupta and Brinkley, 1998; Asprion et al., 2001, 2003a, 2003b; Xu et al., 2004; Ma et al., 2005; Zhu et al., 2006, 2007; Ding et al., 2011), especially the NMR spectroscopy has been become increasing popular (Eckert et al., 1986; Karachewski et al., 1989, 1991; Tkadlecová et al., 1995, 1999; Choi and Tedder, 1996, 1997; Eblinger and Schneider, 1996; Bich et al., 2002; Dohnal and Tkadlecová, 2002; Shekaari et al., 2003; Xu et al., 2005a, 2005b, 2010; Richardson et al., 2006; D'Agostino et al., 2011; Klingenfus and Palmas, 2011), because it allows one to probe mixture behavior on the molecular level. Some relationships between NMR spectroscopy and thermodynamic

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properties of the associated systems have been established. For example, in our previous work, the VLE data of alcohol + hydrocarbon systems were predicted by using the ^{1}H NMR chemical shifts and one activity coefficient at infinite dilution or azeotropic point (Xu et al., 2005b, 2010). Two energy parameters were needed to predict the VLE data in this method, the one was obtained from the ^{1}H NMR chemical shifts and another from the activity coefficient at infinite dilution or azeotropic point of the system. Although the above method could be used to quantitatively predict the VLE data, it was usually limited by other physical properties of the system such as the activity coefficient at infinite dilution, and the direct relations between the NMR spectroscopy and VLE property were not established (Xu et al., 2005b, 2010). Therefore, it is interesting and important to develop an efficient method to predict VLE data from NMR spectroscopic information directly.

In this paper, we try to predict VLE data of alcohol + hydrocarbon systems from NMR spectroscopic information directly. In order to obtain more detailed microstructure information of alcohol + hydrocarbon systems, the ^{1}H NMR chemical shifts of alcohol + hydrocarbon systems over the whole concentration range at 298.15 K were measured by the internal reference method (Zhang et al., 2004; Xu, 2005). The concentration dependence of OH ^{1}H NMR chemical shifts of alcohol and CH ^{1}H NMR chemical shifts of hydrocarbon in the above binary systems were correlated by the local composition model (LC) (Deng et al., 2003) with only one energy parameter, respectively. Using the energy parameters obtained from spectroscopic information, the isothermal and isobaric VLE data of alcohol + hydrocarbon systems were predicted and compared with the experimental values from literatures.

2. Materials and methods

Methanol (purity > 99.9%), ethanol (purity > 99.8%), 1-propanol (purity > 99.7%), 1-butanol (purity > 99.8%), 1-pentanol (purity > 99.5%), 1-hexanol (purity > 99.5%), hexane (purity > 99.5%), cylcohexane (purity > 99.9%), and benzene (purity > 99.7%) were obtained from Aladdin Reagent Co. Ltd., Shanghai, China and used as supplied. Alcohol + hydrocarbon binary mixtures were prepared gravimetrically using an electronic balance (Satorius, the uncertainty was about 0.1 mg). The uncertainty of the mole fraction of the components in the mixtures was estimated to be within 5×10^{-4}.

The internal reference method was adopted to obtain the concentration-dependent chemical shifts of protons (Zhang et al., 2004; Xu, 2005), including the OH group of alcohol and CH group of hydrocarbon (for hexane, CH denotes the terminal methyl group). To avoid the influence of deuterated reagents, a 2-mm capillary tube, in which the deuterated chloroform ($CHCl_3$-*d*) was sealed, which was placed at the center of a 5-mm sample tube filled with the chemical shift reference of tetramethylsilane (TMS) and the sample solutions. It is demanded that the inner capillary tube should be kept parallel with the exterior sample tube. The NMR spectra were obtained using a Bruker AV-400 MHz spectrometer at 298.15 ± 0.1 K and the experimental data for alcohol + hydrocarbon binary systems have been shown in Table S1 in the Supplementary Information.

3. Theory

Based on the Wilson's assumption, Deng et al. (2003) proposed a simple semi-empirical physical model to successfully correlate ^{1}H NMR chemical shift data of mixtures, which could be simply expressed as follows:

$$\delta_{i,obs}=\delta_i^0\Phi_{ii}+\delta_i^\infty\Phi_{ji} \tag{1}$$

where Φ_{ii}, Φ_{ji} are local volume fractions of molecule i and j around central molecule i, respectively. δ_i^0, δ_i^∞ are pure substance and infinitely dilute chemical shifts of molecule i, respectively. They are defined as follows: for any component molecule i ($i=1$ or 2) in a binary solution, when surrounded by the same molecule completely, the measured chemical shift is defined as the pure substance chemical shift. When surrounded totally by different molecules, the measured chemical shift is defined as the infinitely dilute chemical shift, usually obtained by extrapolating the dilute chemical shift to zero concentration (Deng et al., 2003; Xu et al., 2005b).

According to the definition of local composition for a binary mixture, the ratios of the probability of finding a molecule j around a central molecule i can be defined in terms of bulk mole fraction and interaction energies (g_{ji}, g_{ii}) between j–i and i–i pairs of molecules (Wilson, 1964; Orye and Prausnitz, 1965)

$$\frac{x_{ji}}{x_{ii}}=\frac{x_j\exp(-g_{ji}/RT)}{x_i\exp(-g_{ii}/RT)} \tag{2}$$

considering the volume influence, if we define

$$\Lambda_{ji}=\frac{v_j^L}{v_i^L}\exp\left[-(g_{ji}-g_{ii})/RT\right] \tag{3}$$

where g_{ji}, g_{ii} are defined the same as Eq. (2). $v_i{}^L$ is the mole volume of i, which can be calculated by the molecular weight and density. Then the local mole volume fractions can be expressed as following:

$$\Phi_{ii}=\frac{x_{ii}v_i^L}{x_{ii}v_i^L+x_{ji}v_j^L}=\frac{x_i}{x_i+\Lambda_{ji}x_j} \tag{4}$$

$$\Phi_{ji}=\frac{x_{ji}v_j^L}{x_{ii}v_i^L+x_{ji}v_i^L}=\frac{\Lambda_{ji}x_j}{x_i+\Lambda_{ji}x_j} \tag{5}$$

Substituting Eqs. (4) and (5) into Eq. (1), then the original Eq. (1) can be rewritten as below:

$$\delta_{i,obs}=\delta_i^0\frac{x_i}{x_i+\Lambda_{ji}x_j}+\delta_i^\infty\frac{\Lambda_{ji}x_j}{x_i+\Lambda_{ji}x_j} \tag{6}$$

Therefore, the chemical shift data of the OH and CH groups of alcohol + hydrocarbon binary systems can be correlated with only one energy parameter through Eq. (6), respectively. Thus the relationships between observed ^{1}H NMR chemical shifts and composition are established.

In Eq. (6), (g_{ji}–g_{ii}) or (g_{ij}–g_{jj}) is the only one optimum parameter. In order to obtain the parameter from the experimental ^{1}H NMR chemical shifts, the following objective function is used. The parameter is obtained when the objective function is minimum

$$O.F.=\left[\frac{1}{m-1}\sum_{i=1}^{m}(\delta_{cal}-\delta_{exp})^2\right]^{1/2} \tag{7}$$

where m is the number of spectroscopic data. δ_{cal} is the calculated chemical shift according to Eq. (6).

At vapor–liquid equilibrium, taking the vapor phase as ideal gas approximately

$$p=x_i\gamma_i p_i^S+x_j\gamma_j p_j^S \tag{8}$$

where p is the vapor pressure of binary system, p_i^S is the vapor pressure of pure component i, which can be calculated by using the Antoine Coefficient from the literature. x_i is the liquid composition of i, and γ_i is the activity coefficient of i in liquid phase, which can be calculated by using the two energy parameters obtained from ^{1}H NMR chemical shifts through the following Wilson equation (Wilson, 1964; Orye and Prausnitz, 1965):

$$\ln\gamma_i=-\ln(x_i+\Lambda_{ji}x_j)+x_j\left(\frac{\Lambda_{ji}}{x_i+\Lambda_{ji}x_j}-\frac{\Lambda_{ij}}{x_j+\Lambda_{ij}x_i}\right) \tag{9}$$