Chemical Engineering Thermodynamics

Intradiffusion, density and viscosity studies in binary liquid systems of acetylacetone + DMF/DMSO/benzene at 303.15 K and 333.15 K☆

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ABSTRACT

Intradiffusion coefficients of acetylacetone (AcAc) and DMF/DMSO/benzene in binary systems over the entire concentration range at 303.15 K were determined by ^{1}H diffusion-order spectroscopy (DOSY) nuclear magnetic resonance (NMR) method based pulse field gradient (PFG). The densities and viscosities of the above three binary systems at 303.15 K were also studied and employed to calculate the excess molar volumes (V^E) and deviations in viscosity ($\Delta\eta$). Besides, experiments were carried out at 333.15 K for the system of AcAc + DMF. The solvent and temperature effect upon the difference in D between enol and keto tautomers, the tautomeric equilibrium and excess properties (V^E and $\Delta\eta$) were discussed as well. Isotherms of V^E as a function of mole fraction of AcAc (x_1) show positive deviations in benzene but negative deviations in DMF and DMSO, whereas isotherms of $\Delta\eta$ as a function of x_1 record positive deviations in DMF but negative in benzene and DMSO. V^E values show more negative and $\Delta\eta$ values are less positive in the system of AcAc + DMF at 333.15 K compared to 303.15 K. The V^E and $\Delta\eta$ were fitted to a Redlich–Kister type equation and the measured results were interpreted concerning molecular interactions in the solutions.

1. Introduction

As members of β-diketones, acetylacetone (AcAc) and its derivatives are always of great interest in experimental and theoretical studies for their importance being not only an excellent chelating reagent in synthesis chemistry but also a typical researching object of the keto–enol tautomerism [1–10]. Many factors such as temperature, pressure, substituent groups and solvent properties, etc. are proved to affect the move of the keto–enol tautomerism [11]. Besides, excess properties of binary mixtures containing AcAc are also studied, which shows different situations when AcAc dissolved in solvents with different polarities [12–18], but mixtures of AcAc with N, N-dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) have not been reported yet. All in all, most of researchers focused on thermodynamic properties of AcAc in the previous work, and few of them have paid attention to dynamic issues until Chen [19] et al. observed the different self-diffusion coefficients of two tautomers in pure AcAc under variable temperatures and pressures by NMR method.

Based on the work mentioned above, the solvent influence upon the diffusive behavior of AcAc was further investigated [20]. Intradiffusion coefficients (D) of enol and keto tautomers of AcAc in four protonic solvents: methanol/ethanol/1-propanol/1-butanol were measured at 303.15 K by application of ^{1}H DOSY PFG NMR method. It is observed that enol diffuses more quickly than keto by 18% or so in pure AcAc for its compact structure by forming the intramolecular hydrogen bond. When dissolved in methanol, the structure is subjected to a great destruction because the strong intermolecular hydrogen bond is formed between AcAc and methanol, and the destruction is alleviated with the chain length of alkanol lengthening. What's more, differences of D between enol and keto are smaller than 18% in methanol while larger than 18% in 1-butanol due to different intermolecular interactions between AcAc and alkanols with different polarities. And the interactions are also verified by excess molar volumes (V^E) and viscosity deviations ($\Delta\eta$) of the binary systems.

As continuation of our work on the solvent dependence, we present here the experimental data on D, V^E and $\Delta\eta$ when mixing AcAc with three aprotic solvents: DMF/DMSO/benzene. In addition, the temperature influence is studied for the system of AcAc + DMF. In a word, we are trying to explore differences of D between enol and keto tautomers of AcAc and to learn which type of molecular interaction would be responsible for these differences.

2. Experimental

2.1. Equipment and materials

Nuclear Magnetic Resonance Spectrometer (Mercury-plus 300; Varian, America), vibrating-tube densimeter (DMA 4500; Anton Paar, Austria), analytical balance (AL 204; Mettler Toledo, Switzerland) and Ubbelohde viscometer (Φ 0.55 mm; Shanghai Glass Instrument Factory, China) were used in experiments.

Dimethyl sulfoxide and benzene with mass purity of 99.9% were purchased from Alfa Aesar Chemical Company; acetylacetone and N, N-dimethyl formamide with mass purity > 99.5% were obtained from Guangzhou Chemical Reagent Factory. All above reagents were directly used without further purification.

2.2. Intradiffusion experiments

In the DOSY PFG NMR experiments [21], self-diffusion coefficients (intradiffusion coefficients) of each component are calculated according to the Stejskal–Tanner formula [22]:

$$S(G_{zi}) = S(0) \exp\left(-D\gamma^2\delta^2(G_{zi})^2(\Delta - \delta/3)\right) \qquad (1)$$

where $S(G_{zi})$ and $S(0)$ are the signal intensities obtained with gradients G_{zi} and 0, respectively, D is the intradiffusion coefficient, γ is the gyromagnetic constant, δ is the gradient pulse duration and Δ is the diffusion delay. The sequence used in our DOSY experiments is a one-shot pulse sequence [23].

The sample was filled into a capillary (o.d. 1.2 mm, i.d. 1 mm) with both ends sealed, and the capillary was inserted and fixed in the middle of 5 mm sample tube full of heavy water with mass purity of 99.96% as the deuterium locking solvent. All the intradiffusion measurements were operated on a Varian Mercury Plus 300 MHz spectrometer with a probe capable of producing the gradient (g) up to 30 G·cm^{-1}. All the samples were non-spinning during the experiment.

The experimental procedure and parameter setting on the NMR spectrometer have been fully illustrated in our previous paper [20]. The temperature was controlled to ± 0.1 K using the air-bath controller on the NMR spectrometer. The overall error of intradiffusion coefficients was estimated to $\pm 5\%$, and the reproducibility was better than $\pm 2\%$. The measured D of each component and the equilibrium constant, K_e, calculated from the experimental data were listed in Tables 1 and 2.

Table 1
Intradiffusion coefficients (D) of DMF and tautomers of acetylacetone (AcAc) and equilibrium constants (K_e) between tautomers at different AcAc concentrations and temperatures, $p = 0.1$ MPa

Mole fraction of AcAc	303.15 K			333.15 K		
	$D \times 10^9/\text{m}^2\cdot\text{s}^{-1}$			$D \times 10^9/\text{m}^2\cdot\text{s}^{-1}$		
	DMF	Enol/keto	K_e	DMF	Enol/keto	K_e
0.0000	1.61	–/–	–	2.30	–/–	–
0.0500	1.63	1.69/1.52	0.51	2.42	2.29/2.12	0.68
0.1000	1.65	1.66/1.45	0.49	2.48	2.35/2.15	0.66
0.3000	1.78	1.58/1.36	0.46	2.66	2.51/2.24	0.59
0.5000	1.69	1.62/1.39	0.36	2.69	2.60/2.40	0.52
0.7000	1.68	1.76/1.44	0.32	2.57	2.62/2.46	0.46
0.9000	1.70	1.86/1.55	0.28	–	–/–	–
0.9500	–	–/–	–	2.55	2.65/2.50	0.38
1.0000	–	1.90/1.60	0.26	–	2.75/2.42	0.40

2.3. Density and viscosity experiments

Densities of the pure liquids and mixtures were measured with an Anton Paar DMA 4500 vibrating-tube densimeter in which the

Table 2
Intradiffusion coefficients (D) of DMSO/Benzene and tautomers of acetylacetone (AcAc) and equilibrium constants (K_e) between tautomers at different AcAc concentrations at 303.15 K, $p = 0.1$ MPa

Mole fraction of AcAc	303.15 K			303.15 K		
	$D \times 10^9/\text{m}^2\cdot\text{s}^{-1}$			$D \times 10^9/\text{m}^2\cdot\text{s}^{-1}$		
	DMSO	Enol/keto	K_e	Benzene	Enol/keto	K_e
0.0000	0.797	–/–	–	2.24	–/–	–
0.0500	0.800	0.757/0.651	0.65	2.26	2.14/2.03	0.13
0.1000	0.799	0.783/0.683	0.64	2.24	2.18/2.06	0.14
0.3000	0.990	0.996/0.846	0.57	2.19	2.07/1.92	0.15
0.5000	1.23	1.27/1.10	0.44	2.13	1.97/1.79	0.18
0.7000	1.35	1.36/1.26	0.36	2.02	1.92/1.66	0.20
0.9000	1.58	1.69/1.39	0.27	1.87	1.76/1.57	0.22
0.9500	1.73	1.82/1.57	0.24	1.86	1.75/1.56	0.24
1.0000	–	1.90/1.60	0.26	–	1.90/1.60	0.26

temperature was controlled automatically within ± 0.01 K. The apparatus was calibrated with the deionized doubly distilled water and dry air. The uncertainty and reproducibility of density measurements were $\pm 5 \times 10^{-5}$ g·cm^{-3} and 1×10^{-5} g·cm^{-3}, respectively.

All binary mixtures were prepared by mass on an analytical balance (AL 204; Mettler Toledo, Switzerland) with an uncertainty of $\pm 1 \times 10^{-4}$ g. The mole fraction of each mixture was obtained with an uncertainty of $\pm 2 \times 10^{-4}$ from the measured masses of the components, and all the mixtures were completely miscible over the whole composition range. The excess molar volumes were calculated from composition-density data with an uncertainty better than ± 0.002 cm^3·mol^{-1}.

Dynamic viscosities of pure liquids and mixtures were measured using an Ubbelohde viscometer which was calibrated with the distilled water (Marsh, 1987). The apparatus was submerged in a thermostatic bath at the required temperature with a resolution of ± 0.01 K. An electrical stopwatch with a precision of 0.01 s was used. At least three readings were taken for the flow time with repeatability within ± 0.05 s, and the results were averaged. Since all flow times were sufficiently slow and the capillary radius (0.55 mm) was far less than its length (105 mm), the kinetic energy and end corrections were found to be negligible, respectively. The dynamic viscosities of the liquid sample are calculated by the following equation [24]:

$$\eta = \frac{\rho t}{\rho_w t_w}\eta_w \qquad (2)$$

where ρ, ρ_w and t, t_w are densities and flow times of the liquid sample and the distilled water, respectively, η_w is the dynamic viscosity of the distilled water at 303.15 K or 333.15 K. The uncertainty of viscosity results was estimated within ± 0.003 mPa·s.

Densities and dynamic viscosities measured for pure DMSO, DMF and benzene were compared to literature values [25–29] listed in Table 3.

Table 3
Comparison of experimental densities, ρ, and dynamic viscosities, η, of pure liquids with literature values

Liquid	T/K	ρ/g·cm^{-3}		η/mPa·s	
		Exptl.	Lit.	Exptl.	Lit.
DMF	303.15	0.93914	0.9395[①]	0.7555	0.754[①]
	333.15	0.91092	0.91064[②]	0.5542	0.5565[③]
DMSO	303.15	1.09048	1.0908[①]	1.7583	1.788[④]
Benzene	303.15	0.86816	0.8682[⑤]	0.5689	0.564[⑤]

[①] Ref. [25].
[②] Ref. [26].
[③] Ref. [27].
[④] Ref. [28].
[⑤] Ref. [29].