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Influence of alkyl group on interactions between carboxylic acid and acetonitrile at different temperatures

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ABSTRACT

In this paper, the influence of alkyl group as well as temperature on interactions between carboxylic acid and acetonitrile were examined using thermodynamics technique. The carboxylic acid used in this study was acetic acid and propionic acid. To explore the utility of carboxylic acid and acetonitrile, we have carried out the interaction studies of carboxylic acid with acetonitrile using density, ρ, and sound velocity, u, measurements of acetic acid, propionic acid, acetonitrile, and their binary systems {acetic acid or propionic acid (x_1) + acetonitrile (x_2)} as function of temperature. The excess molar volumes, V_m^E, isentropic compressibility, κ_s, and deviation in isentropic compressibility, $\Delta\kappa_s$, were calculated from thermophysical properties, respectively which provide information about the intermolecular interactions as well as the influence alkyl group and temperatures that occurs between carboxylic acid and acetonitrile mixtures. The Redlich–Kister polynomial equation was used to fit the thermodynamics properties to test the experimental data. These results are useful for describing the intermolecular interactions; developing structure–property correlation and molecular modeling that exist between the carboxylic acid and acetonitrile mixtures.

1. Introduction

A wide range of application of acetonitrile is due to its good properties such as superior UV absorbance, unmatched solubilizing properties among other solvents, relatively high dielectric constant, ability to dissolve electrolytes, miscibility with varieties of other solvents, low toxicity, low viscosity and low chemical reactivity. Although the world is seriously working on ways to reduce over reliance on acetonitrile for industrial, pharmaceutical and academic purposes, acetonitrile still remains a versatile organic solvent with diverse application areas. These include its uses in analytical and purification methods in the laboratory settings, purification in refineries, in battery applications, in cyclic voltammetry, in the manufacture of DNA oligonucleotides synthesis and manufacturing of drug substances and products, photographic films, amongst others [1–3].

With increasing awareness on the need to reduce reliance on acetonitrile, it is noteworthy that innovations and optimization of perfect replacements for acetonitrile require a good understanding of acetonitrile interactions in solutions with other solvents and materials [4,5]. This knowledge is necessary to uncover the factors responsible for its properties and reactivity in several chemical and physical environments [6,7]. It is also crucial to achieving the all-important specificity in application situations.

As a result, the intermolecular interactions of acetonitrile have been a subject of research in the recent years with much emphasis on hydrogen bonding [4,8–12]. Moreover, several experimental findings and theoretical calculations have been used to support the proposition that acetonitrile is capable of being a hydrogen bonding acceptor both by that the lone pair of electron on nitrogen atom as well as by the triple bond on the nitrile moiety [8] in Fig. 1. Although many qualitative and quantitative information about hydrogen bonding of acetonitrile has being reported, none has being on acetonitrile-organic acid systems.

Apparently, knowledge of thermo-physical properties is essential tools for microscopic level interactions of liquid mixtures because they provide valuable information about intermolecular interactions which occurs between unlike molecules [13–15]. Thermophysical data of systems are used to calculate the thermodynamic properties which are paramount to designing future pro-

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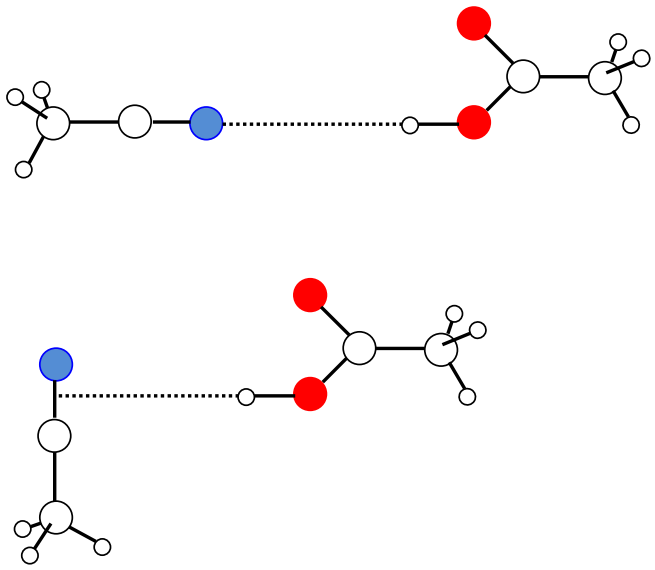

Fig. 1. Schematic representations of possible configurations for the interaction of acetonitrile with ethanoic acid.

cesses and equipment involving these systems [13–15]. It follows that, a deep knowledge of the thermophysical properties of mixed solvent systems of acetonitrile is extremely important if the scientific community will find perfect replacements for acetonitrile in some of its application areas.

The separation of carboxylic acids from hydrocarbons using acetonitrile, a relatively inert and inexpensive solvent, needs the knowledge of their thermodynamic and thermophysical properties which are useful for obtaining information on the intermolecular interactions and geometrical effect in the systems.

The present work is an attempt to understand the intermolecular interactions as well as effects of temperature on physicochemical properties of the acetonitrile, organic acid and their binary mixtures. In this regard, the densities, and speed of sound for acetonitrile, organic acids, acetonitrile and their binary systems {acetic or propionic acid (x_1) + acetonitrile (x_2)} were measured systems over a complete mole fraction range at various temperatures. A literature survey has been done and reveals that no data is available for the investigated systems. These data have a potential to add in developing structure–property correlation and molecular modeling. The present work is a part of our investigations on physicochemical properties of binary systems [16–26].

This study will shed more light on the intermolecular interaction of this widely used organic solvent and it will contribute to the ever growing data on intermolecular interactions occurring in its mixtures with other solvents.

2. Experimental

2.1. Chemicals

The chemical such as acetic acid (CAS # 64-19-7), propionic acid (CAS # 79-09-4), acetonitrile (CAS # 75-05-8), were purchased from Sigma–Aldrich Chem. with purity of ⩾0.99. The mass percent water content was determined using a Metrohm 702 SM Titrino Metter before the experiments, and was found to be 0.03% in acetic acid, 0.02% in propionic acid, and 0.10% in acetonitrile which reported in our previous publications [26–28]. The chemicals were degassed with ultrasound, kept out of the light over 0.3 nm molecular sieves for several days. Comparison with available literature for pure chemical properties such as density and sound velocity has been done in our previous publications [26–28]. The providers and characteristics of the used chemicals are summarized in Table 1. These chemicals were not required for further purification.

2.2. Apparatus and procedure

An OHAUS analytical balance was used to prepare the binary mixtures with a precision of ±0.0001 g. The estimated error in the mole fraction was ±0.0004. The details of the experimental procedure can be found elsewhere [27]. A binary test system (diethyl carbonate + ethanol) [29] was done at 298.15 K, to validate the experimental technique [27]. Our results show that the difference between the experimental and literature was within the experimental error.

The density and speed of sound for pure acetic acid, propionic acid, acetonitrile, and their binary mixtures were measured using digital vibrating-tube densimeter and sound velocity analyzer Anton Paar (DSA 5000 M) in the temperature range of 293.15 to 343.15 K, with an accuracy of ±0.02 K and at atmospheric pressure. The uncertainty in density and speed of sound measurements were less than $\pm 9 \times 10^{-4}$ g cm^{-3} and ±0.8 m s^{-1}, respectively. The speed of sound was measured using a propagation time technique with frequency around 3 MHz [30]. The details about the speed of sound measurements can be found elsewhere [28]. The estimated uncertainty in excess molar volume, isentropic compressibility, and deviation in isentropic compressibility was ±0.005 cm^3 mol^{-1}, $\pm 2 \times 10^8$ Pa^{-1} and $\pm 0.7 \times 10^8$ Pa^{-1}, respectively.

3. Results and discussion

3.1. Thermophysical properties

3.1.1. Density

The density, ρ, was measured for the acetic acid, propionic acid, acetonitrile, and their binary systems {acetic acid or propionic acid (x_1) + acetonitrile (x_2)} at 293.15, 298.15, 303.15, 308.15 and

Table 1
Pure component specifications: suppliers, CAS number, water content specified purity and GC purity.

Chemical name	Supplier	CAS no.	Purification method	Water content Mass fraction purity		
				Mass percent	Initial	GC analysis
Acetic acid	Aldrich	64-19-7	Degassed by ultrasound, kept out of the light over Fluka 0.3 nm molecular sieves for several days; water content were checked before and after by Karl–Fischer titration	0.03	⩾0.99	>0.99
Propanoic acid	Aldrich	79-09-4	Degassed by ultrasound, kept out of the light over Fluka 0.3 nm molecular sieves for several days; water content were checked before and after by Karl–Fischer titration	0.02	⩾0.995	>0.995
Acetonitrile	Aldrich	75-05-8	Degassed by ultrasound, kept out of the light over Fluka 0.3 nm molecular sieves for several days; water content were checked before and after by Karl–Fischer titration	0.10	⩾0.99	⩾0.99

The mass percent water content was determined using a Metrohm 702 SM Titrino Metter before the experiments.