Acoustic and ^{1}H NMR responses of an acidic nuclear extractant with some polar liquids

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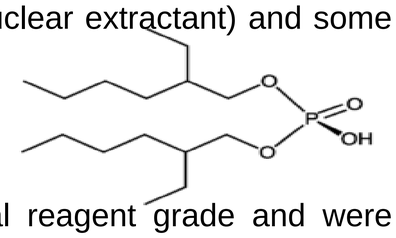
OBJECTIVE

Study of molecular interaction between components of binary liquid mixtures, involving D2EHPA (an acidic nuclear extractant) and some polar liquids (monocarboxylic acids).



D2EHPA ($C_{16}H_{35}O_4P$)

INTRODUCTION

➢The chemicals used were of analytical reagent grade and were purified by standard procedures. All mixtures were prepared by mass using a digital balance with a precision of 1×10^{-6} kg.

➢Ultrasonic velocity, density and viscosity of binary mixture of di-(2-ethyl hexyl) phosphoric acid (D2EHPA) with some polar liquids, i.e acetic acid, propionic acid and n-butyric acid have been experimentally measured over entire range of composition at 2 MHz, temperature 303.15K and at pressure 0.1MPa.

➢The temperature of the sample was controlled by circulating water from an electronically controlled thermostatic water bath to an accuracy of ± 0.1K.

➢The experimental results are employed to compute relaxation time, molecular association constant, deviations in intermolecular free length, free volume, acoustic impedance and excess Gibb's energy of activation of viscous flow and excess enthalpy over entire mole fraction range (X_2) of D2EHPA. The above deviation / excess function were fitted to Redlich-Kister equation to estimate binary coefficients and standard errors.

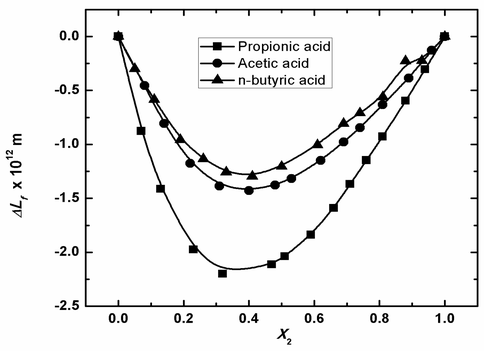
➢The chemical shifts in ^{1}H NMR, a measure of electron density about the probe nuclei, were used to explain the molecular interaction in the three binary liquid mixtures.

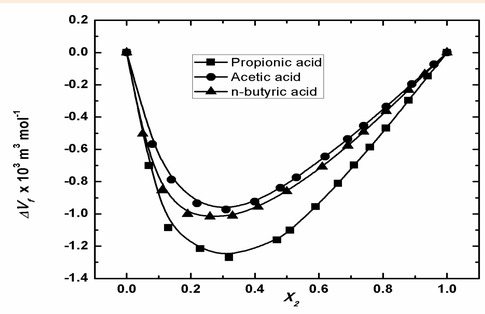
➢The chemical shift of hydrogen atoms in – OH and – OCH_2 of pure D2EHPA and corresponding deviations in chemical shift of the same hydrogen atoms of D2EHPA on mixing with individual acids were observed.

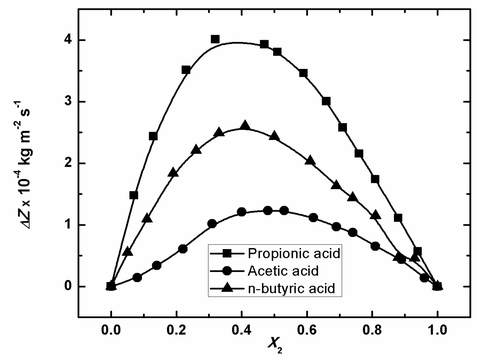
ACOUSTIC RESULT

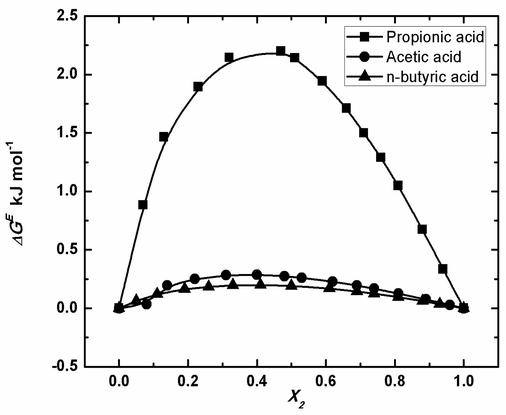
➢It is observed that the values of ultrasonic velocity, U, and viscosity, η increases while density, ρ decreases nonlinearly with increase in D2EHPA mole fraction (X_2). The calculated values of derived parameters show a non-linear increasing/ decreasing trend with mole fraction of D2EHPA in all the three binary mixtures.

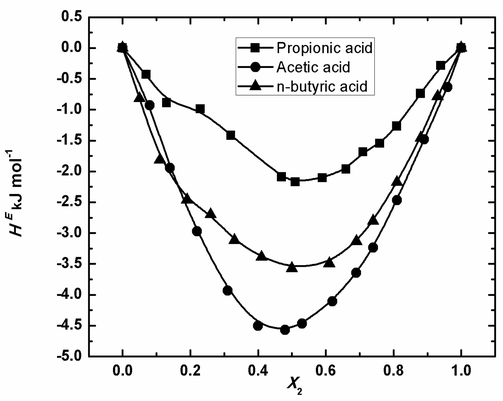
➢ The deviations in the physical property from its ideal behaviour is a measure of the degree of interaction. It may be qualitatively inferred that the interaction between unlike molecules is mainly due to hydrogen bonding through highly polar lone pair oxygen atom of P = O group of D2EHPA and hydrogen atom of -OH group of monocarboxylic acids. Results of the deviation functions show that molecular interaction is stronger in propionic acid mixture at about 0.4 mole fraction of D2EHPA from other two mixtures.





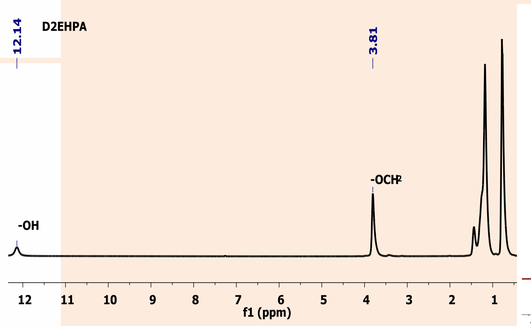


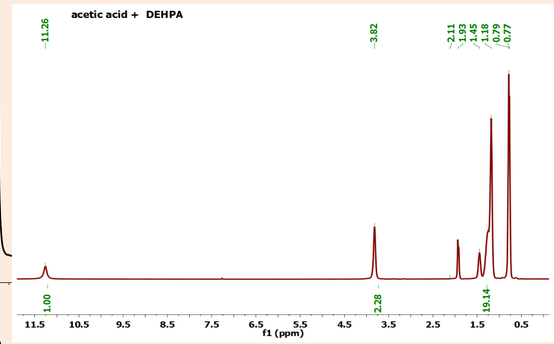




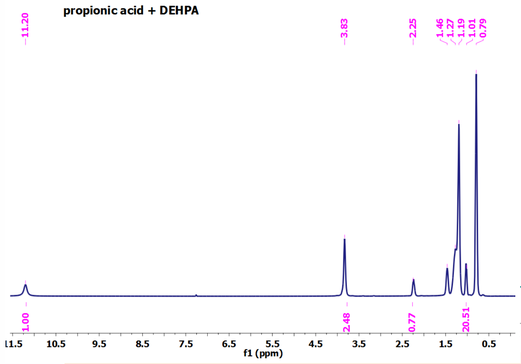
^{1}H NMR RESULT

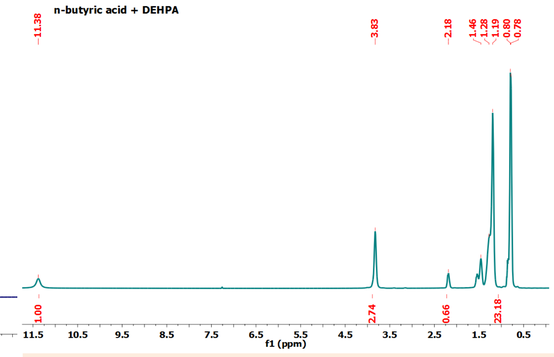
The values of chemical shift in monocarboxylic acids + D2EHPA mixtures have been used to explain molecular interaction in liquid systems. Chemical shifts depend on concentration, temperature and polarity of the components. The observed chemical shift of hydroxyl (-OH) group and carbonyl (-OCH_2) group of pure D2EHPA and its binary mixtures with monocarboxylic acids at a constant volume (acids:D2EHPA :: 1:9) are presented below.





Group	Chemical Shift (ppm)
-OH	12.14
-OCH_2	3.81





➢ The deviation in chemical shifts of hydroxyl group follows the order: propionic acid > acetic acid > n-butyric acid by taking DEHPA as one component. Among three binary mixtures, propionic acid + D2EHPA mixture shows relatively larger deviation in chemical shift that means stronger interaction between unlike molecules.

➢Results of ^{1}H NMR spectra of D2EHPA and acid mixtures are in agreement with that of the macroscopic one obtained from acoustic studies. Therefore, propionic acid may be used as an effective modifier with D2EHPA in the solvent/ nuclear extraction process.

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