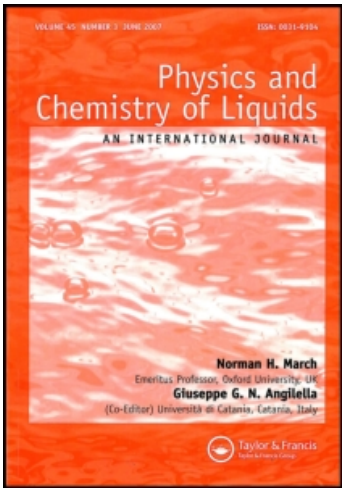

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Ultrasonic and sonochemical reaction studies of *O*-Cresols in different solvent mixtures

S. V. Ranga Nayakulu[a]; S. Venkateswar[b]; C. Sreenivasa Reddy[c]; D. Linga Reddy[c]
[a] Department of Physics & Electronics, T.J.P.S. College, Guntur, 522 006 AP, India [b] Chemical Reaction Engg. Lab, College of Technology, Osmania University, Hyderabad, 500 007 AP, India [c] Department of Physics, University College of Sciences, Osmania University, Hyderabad, 500 007 AP, India

To cite this Article Nayakulu, S. V. Ranga , Venkateswar, S. , Reddy, C. Sreenivasa and Reddy, D. Linga(2006) 'Ultrasonic and sonochemical reaction studies of *O*-Cresols in different solvent mixtures', Physics and Chemistry of Liquids, 44: 3, 269 — 273
To link to this Article: DOI: 10.1080/00319100500337179
URL: http://dx.doi.org/10.1080/00319100500337179

Physics and Chemistry of Liquids
Vol. 44, No. 3, June 2006, 269–273

Taylor & Francis
Taylor & Francis Group

Ultrasonic and sonochemical reaction studies of *O*-Cresols in different solvent mixtures

S. V. RANGA NAYAKULU*†, S. VENKATESWAR‡,
C. SREENIVASA REDDY§ and D. LINGA REDDY§

†Department of Physics & Electronics, T.J.P.S. College, Guntur, 522 006 AP, India
‡Chemical Reaction Engg. Lab, College of Technology, Osmania University, Hyderabad, 500 007 AP, India
§Department of Physics, University College of Sciences, Osmania University, Hyderabad, 500 007 AP, India

(*Received 20 December 2005*)

Ultrasonic and sonochemical reaction studies have been carried out by measuring ultrasonic velocities (v) in the mixing of phenols like *ortho*-cresol with esters like ethyl acetate and iso amyl acetate as solvents. The ultrasonic velocities (v) were measured using ultrasonic pulse echo overlap technique (model UX4400-M) on mixing of *o*-cresol with solvents at different temperatures. The results are interesting because increase in the acid content in the binary mixture decreases the ultrasonic velocity (v). Another important feature is the effect of solvents like isoamyl acetate instead of ethyl acetate on the kinetic process. The reaction rate is larger with ethyl acetate as compared to the kinetic rate in isoamyl acetate. The variation of ultrasonic velocity (v) in the binary mixtures of *o*-cresol–isoamyl acetate system with sonic waves is also studied and it has been found that the reaction rate decreases due to the passage of sonic waves through the medium. Arrhenious parameters have been computed for *o*-cresol–isoamyl acetate system. The free energy of activation ($\Delta F^{\#}$) has been computed for *o*-cresol–ethyl acetate system. It is found that heat of activation (E_a), entropy of activation ($\Delta S^{\#}$) and free energy of activation ($\Delta F^{\#}$) are quite in order for this process.

Keywords: Ultrasonic velocity; Ultrasonic Pulse echo Overlap Technique; *O*-Cresol; Arrhenious parameters; Binary mixtures

1. Introduction

Ultrasound is a useful tool in nearly every case and power ultrasound having frequency between 20 and 100 kHz has been found to have a profound influence on many reactions. It can accelerate reactions, permit the use of unpurified solvents and reagents, replace phase transfer catalysts, permit the reaction to occur under milder conditions and in some cases, even change the reaction path way [1].

Many researchers [2–9] carried out work on the chemical effect of ultrasound and its implications. Taner Tekin *et al*. [10] performed ultrasonic reaction studies in nitric acid

*Corresponding author. Tel.: 0863-2254795. Email: Nayakulu@rediffmail.com

Physics and Chemistry of Liquids
ISSN 0031-9104 print: ISSN 1029-0451 online © 2006 Taylor & Francis
DOI: 10.1080/00319100500337179

with phosphate rock mixtures. The reaction was found to be first order with respect to H^+ and activation energy equal to 16 kJ mol^{-1}. In the present investigation, an attempt has been made to understand the implication of change in ultrasonic velocities with structural change in organic components.

2. Experimental

The chemicals used in the present study were AR grade, obtained from Sd fine chemicals Ltd., Bombay, India. The liquids are thoroughly distilled to remove dissolved impurities using standard chemical procedures. By taking two liquids in separate burettes, job's method of continuous variation has been used to prepare the mixtures of required proportions.

The ultrasonic velocity measurements are made with the help of microprocessor based ultrasonic pulse echo system (Model UX 4400-M) with built in time, velocity and thickness measuring feature, with a frequency of 2 MHz supplied by Roop Telsonic Ultrasonic Ltd., Bombay, India. The internal circuit of ULTRASONIX 4400 M is designed with full solid state structure. Further outstanding stability and reliability of operation is ensured by dynamic use of integrated circuit and PCB mounted gold plated switches. It has special memory features which enables one to enter testing procedures like angle and type of transducers etc. for permanent storage and direct digital read out of velocity of the samples and attenuation coefficient of the samples. The accuracy of the instrument in measuring velocity is ± 1 m s^{-1}.

The neutral components are taken at thermostated temperature and the reactive component is added quickly and the variation of ultrasonic velocities is measured with reference to time. The infinity value of ultrasonic velocity (v_∞) is taken as the final value, which does not change. Soon after mixing the ultrasonic velocities is measured and is taken as velocity at zero time (v_0).

Sonotrode converter (Model SE 26/20) having frequency of 36 kHz was introduced into the medium. Sonic waves were allowed to pass into the medium for few minutes and corresponding changes in ultrasonic velocities have been observed and recorded.

3. Computation

(i) The following rate equation is used to determine the first-order rate constants [11]

$$k = \frac{2.303}{t} \log\left(\frac{v_\infty - v_0}{v_\infty - v_t}\right) \tag{1}$$

where, 't' is the time, 'v_∞' is the infinity value in ultrasonic velocities, which does not change; 'v_0' is the velocity at zero time and 'v_t' is the velocity at a particular time, respectively.

Thermodynamic parameters are evaluated as follows:

(ii) Enthalpy of activation ($\Delta H^\#$) can be computed [12] as follows:

$$\Delta H^\# = E_a - RT \tag{2}$$

where, 'E_a' is the energy of activation, $\Delta H^{\#}$ is the enthalpy of activation, R is the universal gas constant and 'T' is thermodynamic temperature.

(iii) Entropy of activation ($\Delta S^{\#}$) can be computed [12] as follows:

$$\Delta S^{\#} = R \ln\left(\frac{k_r h}{kT}\right) + \frac{\Delta H^{\#}}{T} \tag{3}$$

(iv) Free energy of activation ($\Delta F^{\#}$) can be obtained [12] as follows:

$$k_r = \left(\frac{kT}{h}\right) e^{-\Delta F^{\#}/RT} \tag{4}$$

where, 'k_r' is reaction rate, 'h' is the Planck's constant, $\Delta F^{\#}$ is the free energy.

4. Results and discussion

Ultrasonic velocity (v) changes with respect to time have been determined at various percentages of ethyl acetate and *o*-cresol at 30°C. Table 1 shows that there is decrease in the first-order rate constants with respect to *o*-cresol with increase in the percentage of *o*-cresol. This means more the acidic the solvent environment is, the movement of ultrasonic waves seems to be lesser. This is in tune with earlier postulates [13]. In table 2 values of free energy of activation ($\Delta F^{\#}$) are given for different solvent percentages of ethyl acetate and *o*-cresol. The values are justifiable as the rate of the reaction at lower percentage of ethyl acetate is lesser than the rate of reaction at higher percentage of the ethyl acetate resulting in higher free energy of activation ($\Delta F^{\#}$).

For purpose of comparison isoamyl acetate has been used in the place of ethyl acetate in the binary mixtures. It is observed that there is a decrease in rate constants as

Table 1. Rate constants (K) of mixing *o*-cresol with ethyl acetate at 30°C temperature.

Percentage of composition		Rate constant (k) (min^{-1})
Ethyl acetate	*o*-cresol	
60	40	0.0492
40	60	0.0392

Table 2. Evaluation of free energy of activation ($\Delta F^{\#}$) of mixture of ethyl acetate and *o*-cresol at 30°C temperature.

Percentage of composition		Free energy of activation ($\Delta F^{\#}$) $J\,mol^{-1}$
Ethyl acetate	*o*-cresol	
60	40	53057.27
40	60	53629.76

Table 3. Rate constants (k) of mixing of binary mixture of isoamyl acetate (40%) and o-cresol (60%) at different temperatures.

Temperature	Rate constants (k) min^{-1}
30°C	0.04395
38°C	0.06729
30°C*	*0.01831

Table 4. Evaluation of thermodynamic parameters of mixture of isoamyl acetate (40%) and o-cresol (60%).

Percentage of composition		Energy of activation (E_a) J mol^{-1}	Enthalphy of activation ($\Delta H^{\#}$) J mol^{-1}	Free energy of activation ($\Delta F^{\#}$) J mol^{-1}	Entropy activation ($\Delta S^{\#}$) J mol^{-1}
Isoamyl acetate	o-cresol				
40	60	504.6	−2014.54	53341.5	−169.95

isoamyl group has a long chain. Obviously, the movement of ultrasonic waves is hindered, when ethyl acetate is changed to isoamyl acetate, which has large hydrocarbon group. Thus it appears that the movement of ultrasonic waves depends on acidity or basicity [10] and the nature of the organic components. The mixing of o-cresol with isoamyl acetate has been done at 38°C. The rate constants at 30°C and 38°C are given in table 3. This experimental has been repeated in the presence of sonic waves to find out the differential effect of prior treatment of the binary mixtures with sonic waves before determining the ultrasonic velocities. This has been referred to as 38°C* in table 3, which shows a decrease in the rate constant when there is prior treatment with sonic waves. This means the equilibrium in the binary mixture is disturbed and due to this disturbance there is a formation of aggregates in each component. Hence the propagation of ultrasonic waves becomes difficult. This is reflected after treating the system with sonic waves. Table 4 contains the derived thermodynamical parameters at 40% isoamyl acetate and 60% o-cresol composition.

5. Conclusion

Ultrasonic and sonochemical studies have been conducted using o-cresol as one of the components and varying the other binary component using ethyl acetate or isoamyl acetate. The results have been rationalized on the basis of structural changes in the organic components and their corresponding variation of acidic nature in the mixture of solvents. Heat of activation, entropy of activation and free energy of activation have been computed. These lead to a better understanding of the mechanism in the process of mixing of solvents.

Acknowledgement

One of the authors S.V. Ranganayakulu is thankful to Prof. S. Radha Krishna Murthy, visiting professor, Nagarjuna University, Nagarjuna Nagar for valuable suggestions.

References

[1] Oliver Dahlem, Vincent Demaiffe, Veronique Halloin, Jacques Reisse. *AIChE J.*, **44**, 2724 (1998).
[2] Makino, Magdi, Masoba, Peter Reisz. *J. Phy. Chem.*, **87**, 1369 (1983).
[3] A.U. Cum, G. Galli, R. Gallo, A. Spadaro. *Ultrasonics*, **32**, 267 (1992).
[4] C.G. Stephans, J.G. Hatiris, D.E. Mourmouras. *Ultrasonics Sonochemistry*, **5**, 33 (2004).
[5] Kenneth S. Suslick. *Sci. Amer.*, **12**, 80 (1989).
[6] W.T. Rechards, A.L. Loomis. *J. Am. Chem. Soc.*, **49**, 3056 (1927).
[7] H. Monnier, A.M. Wilhelm, H. Delmas. *Ultrasonics Sonochemistry*, **6**, 67 (1999).
[8] A. Tuulmets, S. Salmar. *Ultrasonics Sonochemistry*, **8**, 209 (2001).
[9] Ph. Moisy, I. Bisel, F. Genvo, F. Rey-Gairez, L. Venault, P. Blanc. *Ultrasonics Sonochemistry*, **8**, 175 (2001).
[10] Taner Tekin, Derya Tekin, Mahmut Bayramosiu. *Ultrasonics Sonochemistry*, **8**, 373 (2001).
[11] Arthus A. Frost, Ralph G. Pearson. *Kinetic & Mechanism*, 2nd Edn, Wiley Eastern Limited (1957).
[12] K.J. Laidler. *Theories of Chemical Reaction Rates*, McGraw Hill Company (1969).
[13] S.V. Ranga Nayakulu, C. Sreenivasa Reddy, D. Linga Reddy. *J. Acous. Soc. India*, **31**, 231 (2003).