

Temperature Dependent Dielectric Relaxation Study of Arvindasava and Pippalyasava (Ayurvedic Medicines) in Ethanol

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ABSTRACT

Temperature dependent Dielectric relaxation study of Ayurvedic medicines, Arvindasava and Pippalyasava in Ethanol has been carried out at sampling frequency 12.4 GHz and at temperatures 10⁰C, 20⁰C, 30⁰C & 40⁰C. Time domain reflectometry (TDR) in reflection mode has been used as a technique. In TDR a fast rising step pulse of 25 ps is incident on the asava kept in the cell. The reflected pulse from the cell is sampled with incident pulse in sampling oscilloscope. The sampled pulses are digitized. The time dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$ using Fourier transformation. The static dielectric constant (ϵ_0), dielectric relaxation time (τ), Bruggeman factor (f_B) and thermodynamic parameters of Ayurvedic medicines, “ asava ” were evaluated from complex reflection spectra.

KEYWORDS

Ayurvedic Medicines, Asava, Dielectric relaxation, Time domain reflectometry, Fourier transformation, Dielectric constant, Relaxation time.

1. INTRODUCTION

Ayurvedic medicines, ‘ASAVA’ are the self generated alcoholic preparation with 10% alcohol and 25% sugar. A variety of medicinal herbs and their leaves, flowers, fruits, peels, roots, gum and resins; gems, metals and colours are used in the production of Ayurvedic medicines. The Sanskrit names of medicinal plants and metals have been used to indicate the standard names of asava. For example, the basic medicinal plant used in the production of Arvindasava is Lotus. The Sanskrit name of Lotus is Arvind.

The solute-solvent molecular interactions between Ayurvedic medicines, ASAVA and associative

solvent Ethanol are presented in this paper. Ayurvedic medicines, ‘ASAVA’ having carbonyl (>C=O) and cyanide (C-N) functional groups are selected to study relative structural changes as well as change in molecular interactions with ethanol molecules.

2. EXPERIMENTAL

Ayurvedic medicines, Arvindasava and Pippalyasava were obtained from Ayurved rasasala, Pune. Ethanol AR grade (Changshu Yangyuan Chemical, China) 99.9% purity was obtained commercially and used without further purification. The solutions were prepared at different volume percentage of Arvindasav in Ethanol and Pippalyasava

in Ethanol in steps of 10 vol. %, within a ± 0.01 % error limit.

The complex permittivity spectra were studied using time domain reflectometry. The Hewlett Packard HP 54750A-sampling oscilloscope with an HP 54754A TDR plug-in module was used. A fast rising step voltage pulse of about 25 ps rise time generated by a tunnel diode was propagated through a flexible coaxial cable. The asava was placed at end of the coaxial line in the standard military application (SMA) coaxial cell of 3.5 mm outer diameter and 1.35 mm effective pin length.

All measurements were done under open load conditions. The change in pulse on reflection from the sample placed in cell was monitored by the sampling oscilloscope. The reflected pulse without sample $R_1(t)$ and with sample $R_x(t)$ were digitized in 1024 points and stored on disc.

The temperature controller system with a water bath and a thermostat has been used to maintain the constant temperature within the accuracy limit of $\pm 1^\circ\text{C}$. The sample cell was surrounded by an insulating container through which, the constant temperature water was circulated.

3. DATA ANALYSIS

The time dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$ using Fourier transformation (Samulon¹; Shannon²) as

$$\rho^*(\omega) = \frac{c p(\omega)}{j\omega d q(\omega)}$$

Where $p(\omega)$ and $q(\omega)$ are Fourier transforms of $(R_1(t)-R_x(t))$ and $(R_1(t)+R_x(t))$, respectively, c is the velocity of light, ω is the angular frequency, and d is the effective pin length.

The complex permittivity spectra $\varepsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by using the bilinear calibration method (Cole^{3,4} et al.). The experimental values of $\varepsilon^*(\omega)$ are fitted with the Debye equation (Cole and Cole³; Davidson and Cole⁵; Havriliak and Negami⁶)

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + j\omega\tau)}$$

with ε_0 , ε_∞ and τ as fitting parameters. A nonlinear least-squares fit method (Bevington⁷) was used to determine the values of dielectric parameters. The values of static dielectric constant (ε_0) and dielectric relaxation time (τ) are listed in table 1 & 2.

The modified Bruggeman⁸ mixture formula, given below, is used to fit experimental data.

$$f_B = \left(\frac{\varepsilon_{om} - \varepsilon_{ow}}{\varepsilon_{os} - \varepsilon_{ow}} \right) \left(\frac{\varepsilon_{os}}{\varepsilon_{om}} \right)^{1/3}$$

$$= 1 - [a - (a - 1) * V] * V = 1 - f(V)$$

with “a” as a fitting parameter and ‘f’ can be interpreted as fraction of effective volume V. The relative change in value of “a” reveals amount of interaction between solute and solvent. The values of Bruggeman factor are listed in table 3 & 4.

Table1: Temperature dependent dielectric parameters for Arvindasava-Ethanol mixture

Vol fra	10 ⁰ C		20 ⁰ C		30 ⁰ C		40 ⁰ C	
	ε ₀	τ ps	ε ₀	τ ps	ε ₀	τ ps	ε ₀	τ ps
0.0	26.8	167.0	25.9	150.7	25.2	128.0	24.5	111.2
0.1	31.3	131.4	30.4	114.2	29.7	99.1	28.3	86.5
0.2	36.1	113.2	35.0	100.9	34.1	86.6	32.2	75.2
0.3	41.9	102.0	40.1	90.8	38.9	78.7	36.9	65.9
0.4	46.8	91.3	45.8	79.0	43.3	71.4	41.2	60.4
0.5	53.2	85.4	51.7	71.1	49.0	63.2	46.9	57.7
0.6	58.0	80.5	56.7	68.3	54.7	56.4	52.1	54.3
0.7	63.9	70.6	61.0	63.5	59.2	54.7	56.9	53.4
0.8	69.4	66.2	66.1	60.5	63.0	53.2	59.9	52.5
0.9	72.6	61.7	71.5	55.4	67.4	52.6	63.5	50.0
1.0	75.2	60.5	72.5	54.5	70.6	51.5	68.2	49.5

Table4: Ideal, experimental & theoretical values of Bruggeman factor (f_B) for Pippalyasava-Ethanol mixture.

vol fra Pip	Ideal	10 ⁰ C a=0.562		20 ⁰ C a=0.438		30 ⁰ C a= 0.526		40 ⁰ C a=0.637	
		exp	the	exp	the	exp	the	exp	the
0.0	1.0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
0.1	0.9	0.94	0.94	0.95	0.98	0.94	0.95	0.93	0.94
0.2	0.8	0.87	0.86	0.89	0.92	0.88	0.88	0.86	0.86
0.3	0.7	0.79	0.81	0.82	0.84	0.80	0.80	0.78	0.79
0.4	0.6	0.70	0.71	0.74	0.73	0.71	0.71	0.69	0.69
0.5	0.5	0.61	0.61	0.64	0.63	0.62	0.61	0.59	0.59
0.6	0.4	0.51	0.52	0.54	0.54	0.51	0.55	0.49	0.48
0.7	0.3	0.39	0.37	0.42	0.39	0.40	0.38	0.38	0.37
0.8	0.2	0.27	0.25	0.29	0.27	0.28	0.25	0.26	0.25
0.9	0.1	0.14	0.14	0.15	0.15	0.14	0.13	0.13	0.13
1.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table2: Temperature dependent dielectric parameters for Pippalyasava-Ethanol mixture

Vol fra	10 ⁰ C		20 ⁰ C		30 ⁰ C		40 ⁰ C	
	ε ₀	τ ps	ε ₀	τ ps	ε ₀	τ ps	ε ₀	τ ps
0.0	26.8	167.0	25.9	150.7	25.2	128.0	24.5	111.2
0.1	32.1	135.8	31.2	115.8	29.8	98.0	28.9	88.7
0.2	36.7	113.9	35.9	98.7	34.3	85.7	33.5	77.2
0.3	42.5	100.9	41.4	87.5	40.0	77.4	38.6	69.2
0.4	49.9	89.6	48.1	78.5	48.3	70.3	43.2	60.7
0.5	54.9	86.1	53.1	71.7	51.2	59.6	48.7	54.9
0.6	60.4	80.1	58.3	65.2	56.7	57.9	53.5	52.8
0.7	66.5	69.0	63.9	59.7	61.5	52.1	59.3	49.3
0.8	69.5	64.4	68.9	58.5	65.6	50.1	62.9	48.7
0.9	74.5	57.9	72.6	53.7	69.9	48.8	67.1	47.4
1.0	78.4	53.5	73.7	52.9	72.9	47.0	70.8	44.3

The thermodynamic parameters molar enthalpy of activation ΔH and the molar entropy of activation ΔS were obtained using equation

$$\tau = \frac{h}{KT} \exp[(\Delta H - T\Delta S) / RT]$$

and are listed in table 5.

Table 5: Activation enthalpy and entropy of Asava-Ethanol mixture for various concentrations.

Volume fraction	Arvindasava + Ethanol		Pippalyasava + Ethanol	
	ΔH KJ/mole	ΔS J ⁰ Kmole	ΔH KJ/mole	ΔS J ⁰ Kmole
0.0	7.6740	-0.0303	7.6740	-0.0303
0.1	7.7990	-0.0297	8.1884	-0.0265
0.2	7.7959	-0.0266	7.17.07	-0.0287
0.3	8.1961	-0.0243	6.7805	-0.0291
0.4	7.3685	-0.0262	6.8988	-0.0277
0.5	7.0928	-0.0264	8.8892	-0.0202
0.6	7.7117	-0.0238	7.6688	-0.0238
0.7	4.8378	-0.0329	6.0169	-0.0285
0.8	3.6371	-0.0366	4.8537	-0.0321
0.9	2.5962	-0.0397	2.6303	-0.0390
1.0	2.3812	-0.0403	2.5442	-0.0391

Table3: Ideal, experimental & theoretical values of Bruggeman factor (f_B) for Arvindasava-Ethanol mixture.

vol fra Arv	Ideal	10 ⁰ C a=0.527		20 ⁰ C a=0.554		30 ⁰ C a= 0.629		40 ⁰ C a=0.703	
		exp	the	exp	the	exp	the	exp	the
0.0	1.0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
0.1	0.9	0.94	0.96	0.94	0.98	0.93	0.94	0.93	0.91
0.2	0.8	0.87	0.90	0.87	0.89	0.86	0.86	0.85	0.84
0.3	0.7	0.79	0.81	0.79	0.79	0.78	0.79	0.76	0.79
0.4	0.6	0.73	0.70	0.71	0.71	0.69	0.71	0.67	0.69
0.5	0.5	0.61	0.61	0.61	0.62	0.59	0.59	0.57	0.58
0.6	0.4	0.50	0.48	0.51	0.50	0.49	0.47	0.47	0.45
0.7	0.3	0.39	0.38	0.39	0.37	0.38	0.37	0.36	0.35
0.8	0.2	0.27	0.24	0.20	0.25	0.26	0.25	0.25	0.24
0.9	0.1	0.14	0.12	0.14	0.13	0.13	0.13	0.13	0.11
1.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

4. RESULT AND DISCUSSION

The static permittivity is measure of effective dipole moment per unit volume in mixture. Relaxation time of biological material can be related to the size of molecule, mobility of molecules in liquid, molecular volume, viscosity, and temperature. Decrease in relaxation time can be correlated to decrease in size of molecule as well as to increase in mobility of molecules in liquid. If the polar solute molecules are spherical, and large by comparison with the solvent molecules, then the orientation relaxation of the solute molecules can usefully be described using Debye's model. In this model the dipolar solute molecules are considered as spheres whose rotation is opposed by the viscosity of the surrounding solvent medium.

When value of numerical fitting parameter "a" is unity, modified Bruggeman mixture formulae reduces to original Bruggeman mixture formulae. Decrease in value of "a" below unity shows increase in effective volume fraction of solvent in mixture.

The value of activation enthalpy (ΔH) gives an idea about nature of compactness in molecules of liquid. The variation in (ΔH) with change in solute concentration provides us information about relative change in amount of hydrogen bonding in mixture.

5. CONCLUSION

The static permittivity increases with addition of ASAVA in ethanol. Decrease in permittivity with increasing temperature is also observed for all concentrations. This raise in permittivity with increasing amount of solute

indicates linear increase in effective dipole moment of the system.

The variation in relaxation time shows that, the decrease in amount of hydrogen bonding between solute and solvent molecules, which leads to smaller molecular structures rotating fast.

The values of numerical fitting parameter 'a' are below unity shows increase in effective volume fraction of solvent in mixture, with decreasing size of ASAVA showing weaker solute solvent interactions.

The activation enthalpy (ΔH) decreases with increase in volume fraction of ASAVA in mixture, which shows decrease in amount of hydrogen bonding between molecules of liquid.

REFERENCES

1. Samulon H.A. Spectrum analysis of transient response curves, *Proc. IRE* 1951,39,175-186.
2. Shannon C.E., Communication in the presence of noise, *Proc. IRE* 1949,37,10.
3. Cole K.S. & Cole R.H. Dispersion and absorption in dielectrics, *J.Chem. Phys.* 1941,9,341-345.
4. Cole R.H.; Berbarian J.G.; Mashimo S.; Chryssikos G.; Burns A.; Tombari E. Time domain reflection methods for dielectric measurements to 10 GHz, *J. Appl. Phys.* 1989,66,793-802.
5. Davidson D.W.; Cole R.H. Dielectric relaxation in Glycerin, *J. Chem. Phys.* 1950,18,1417.
6. Havriliak S. & Negami S. A complete plane analysis of α -dispersion in some polymer systems *J. Polym. Sci. Polym. Symp.* 1966,99-117.
7. Bevington P. R., *Data reduction and error analysis for the physical sciences*; McGraw Hill: New York, 1969.
8. Bruggeman D.A.G., *Ann. Phys.* (Leipzig) 5 (1935) 636.