882 *J. Chem. Eng. Data* **2006,** *51,* 882−885

Dielectric Relaxation of Propan-1-ol with Chlorobenzene, 1,2-Dichloroethane, and Dimethylene Chloride at (288, 298, 308, and 318) K Using Time-Domain Reflectometry Technique

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The values of complex permittivity of molecules containing chlorine with propan-1-ol binary mixtures have been determined over the frequency range of (0.1 to 20) GHz, at temperatures of (288, 298, 308, and 318) K, using the time-domain reflectometry (TDR) method for 11 molalities of each molecule containing chlorine with propan-1-ol system. The dielectric relaxation in these systems can be described by a single relaxation time using the Havriliak and Negami model. The static dielectric constant (ϵ_0) and relaxation time (τ) have been obtained by fitting experimental data with the Havriliak−Negami equation.

Introduction

This work is part of an extensive study of the dielectric properties of fluid mixtures when one of the components is an alcohol.[1−5] These other types of molecules may be associative like formamide, *N*-methyl formamide, dimethyl formamide,[6,7] etc. or nonassociative like dimethyl formamide,[8] acetonitrile,[9,10] etc. No microscopic information can be extracted from macroscopic measurements without recourse to a statistical mechanical model. Previously, we reported the effect of molecules with chlorine mixed with an alkanol[11−13] and continue this work here. The chlorine molecules are chlorobenzene (CB), 1,2-dichloroethane (DE), and dimethylene chloride (DC) mixed with propan-1-ol (PR).

Experimental Section

Propan-1-ol, chlorobenzene, 1,2-dichloroethane, and dimethylene chloride were purchased from Qualigens Fine Chemicals Pvt. Ltd., Bombay, India. Their GC analysis indicated a mol % purity of 99.5, 99.0, 99.0, and 99.0, respectively. All the samples were used without further purification. The solutions were prepared at 11 different volume percentages of propan-1-ol (ϕ_1) in chlorine molecules in steps of 10 %, within 0.02 % error limit. Using these volume percents, the mole fraction is calculated as

$$x_1 = (\upsilon_1\rho_1/m_1)/[(\upsilon_1\rho_1/m_1) + (\upsilon_2\rho_2/m_2)] \qquad (1)$$

where m_i, υ_i, and ρ_i represent the molecular weight, volume percent, and density of the ith (i = 1, 2) liquids, respectively.

The complex permittivity spectra were obtained with a time-domain reflectometer[14−16] similar to that described by Cole et al.[14] The Hewlett Packard HP 54750 sampling oscilloscope with a HP 54754A TDR plug-in module were used. A fast rising step voltage pulse with a rise time of about 39 ps was generated by a tunnel diode and propagated through a coaxial line. The transmission line under test was placed at the end of coaxial line and interconnected with a standard military applications (SMA) coaxial connector with 3.5 mm o.d. and 1.35 mm effective pin length. All measurements were performed under open-load conditions. The change in the pulse after reflection from the sample placed in the cell was monitored by the sampling oscilloscope. A sampling time window of 5 ns was

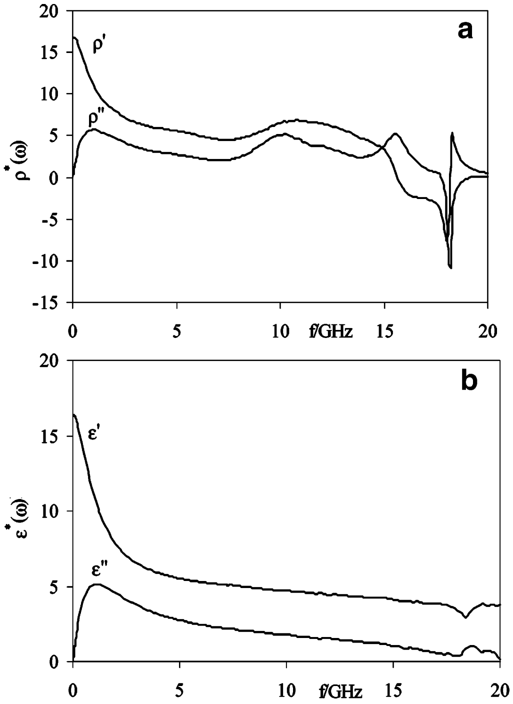

Figure 1. (a) $\rho^*(\omega)$ spectrum for propan-1-ol + dimethylene chloride mixture for x_1 = 0.4615 and T = 298 K. (b) $\epsilon^*(\omega)$ spectrum for propan-1-ol + dimethylene chloride mixture for x_1 = 0.4615 and T = 298 K.

Table 1. Comparison of Data for the Liquids Used with Literature Values at 298 K

	ϵ_0		ρ/(g·cm^{-3})	
liquid	this work	lit[a]	this work	lit[a]
propan-1-ol	20.73	20.1	0.803	0.8035
chlorobenzene	5.54	5.621	1.105	1.107[b]
1,2-dichloroethane	10.43	10.40[c]	1.325	1.325
dimethylene chloride	8.51	8.8[b]	1.323	1.325

[a] Ref 24. [b] Ref 26. [c] Ref 14.

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10.1021/je0503397 CCC: $33.50

Table 2. Temperature-Dependent Dielectric Relaxation Parameters for Propan-1-ol (1) + Chlorobenzene (2), Propan-1-ol (1) + 1,2-Dichloroethane (2), and Propan-1-ol (1) + Dimethylene Chloride (2)[a]

x_1	$T = 288$ K	$T = 298$ K	$T = 308$ K	$T = 318$ K	x_1	$T = 288$ K	$T = 298$ K	$T = 308$ K	$T = 318$ K
Propan-1-ol (1) + Chlorobenzene (2)									
ϵ_0									
0.0000	5.94 (0)	5.54 (0)	5.51 (0)	5.33 (0)	0.6740	17.4 (5)	16.6 (4)	15.9 (3)	15.1 (4)
0.1314	7.1 (7)	6.9 (3)	6.7 (4)	6.6 (3)	0.7606	19.0 (4)	18.2 (3)	17.3 (2)	16.4 (0)
0.2540	8.9 (7)	8.5 (6)	8.1 (4)	7.8 (5)	0.8449	20.2 (4)	19.3 (4)	18.3 (2)	17.3 (5)
0.3685	11.5 (6)	10.8 (5)	10.3 (5)	9.7 (3)	0.9246	21.2 (5)	20.1 (7)	19.1 (4)	17.9 (8)
0.4759	13.6 (4)	12.8 (8)	12.2 (3)	11.5 (6)	1.0000	21.97 (0)	20.73 (0)	19.65 (0)	18.09 (0)
0.5766	15.5 (4)	14.7 (4)	13.9 (3)	13.2 (2)					
τ (ps)									
0.0000	13.84 (0)	13.78 (0)	13.09 (0)	13.02 (0)	0.6740	211.0 (3)	169.0 (6)	141.0 (0)	121.7 (2)
0.1314	25.8 (5)	24.5 (5)	21.4 (4)	21.3 (4)	0.7606	245.8 (1)	196.0 (4)	160.4 (5)	139.0 (4)
0.2540	46.7 (8)	42.1 (5)	38.3 (4)	34.2 (6)	0.8449	277.0 (0)	222.0 (4)	179.0 (6)	156.0 (3)
0.3685	93.0 (6)	79.7 (6)	70.0 (4)	58.0 (5)	0.9246	305.0 (6)	247.0 (4)	198.0 (3)	170.0 (2)
0.4759	133.0 (7)	112.0 (5)	95.4 (5)	81.0 (5)	1.0000	330.82 (0)	272.61 (0)	215.73 (0)	178.77 (0)
0.5766	173.0 (5)	139.0 (5)	118.1 (7)	100.0 (4)					
g^{eff}									
0.0000	0.50	0.45	0.46	0.44	0.6740	1.75	1.72	1.69	1.65
0.1314	0.66	0.65	0.64	0.64	0.7606	1.88	1.85	1.81	1.75
0.2540	0.88	0.85	0.82	0.80	0.8449	1.96	1.93	1.87	1.82
0.3685	1.18	1.13	1.10	1.05	0.9246	2.01	1.96	1.92	1.84
0.4759	1.40	1.35	1.31	1.27	1.0000	2.03	1.97	1.92	1.81
0.5766	1.58	1.54	1.49	1.45					
Propan-1-ol (1) + 1,2-Dichloroethane (2)									
ϵ_0									
0.0000	10.88 (0)	10.43 (0)	10.10 (0)	9.82 (0)	0.6153	18.8 (6)	17.8 (0)	16.9 (3)	15.6 (2)
0.1059	11.1 (1)	10.6 (1)	10.4 (3)	10.3 (6)	0.7133	19.9 (7)	18.9 (7)	18.2 (2)	16.8 (2)
0.2104	11.4 (1)	11.1 (6)	10.9 (2)	10.5 (8)	0.8100	20.8 (4)	19.7 (5)	18.8 (2)	17.6 (3)
0.3136	13.3 (7)	12.7 (6)	12.1 (6)	11.6 (3)	0.9056	21.3 (3)	20.2 (4)	19.2 (3)	18.0 (3)
0.4155	15.5 (0)	14.5 (5)	13.6 (5)	12.8 (2)	1.0000	21.97 (0)	20.73 (0)	19.65 (0)	18.09 (0)
0.5160	17.3 (1)	16.3 (3)	15.4 (0)	14.2 (2)					
τ (ps)									
0.0000	11.47 (0)	10.71 (0)	10.12 (0)	9.92 (0)	0.6153	158.0 (2)	128.3 (7)	108.6 (4)	89.0 (3)
0.1059	18.8 (3)	17.5 (8)	16.9 (2)	14.7 (4)	0.7150	201.3 (3)	161.4 (2)	135.2 (1)	113.0 (3)
0.2104	28.1 (7)	25.3 (6)	22.9 (0)	21.0 (8)	0.8100	242.2 (4)	192.8 (6)	161.9 (3)	134.3 (1)
0.3136	57.4 (0)	48.2 (4)	41.6 (2)	33.4 (1)	0.9056	287.7 (2)	229.2 (6)	188.3 (5)	158.3 (6)
0.4155	86.9 (7)	70.2 (6)	60.4 (1)	47.4 (5)	1.0000	330.82 (0)	272.61 (0)	215.73 (0)	178.77 (0)
0.5160	119.8 (3)	96.7 (4)	81.5 (7)	64.6 (8)					
g^{eff}									
0.0000	0.64	0.63	0.62	0.62	0.6153	1.47	1.43	1.39	1.32
0.1059	0.67	0.66	0.67	0.66	0.7150	1.63	1.59	1.55	1.48
0.2104	0.72	0.72	0.73	0.72	0.8100	1.77	1.73	1.69	1.63
0.3136	0.90	0.88	0.87	0.84	0.9056	1.89	1.85	1.80	1.73
0.4155	1.10	1.06	1.01	0.97	1.0000	2.03	1.97	1.92	1.81
0.5160	1.29	1.25	1.21	1.14					
Propan-1-ol (1) + Dimethylene Chloride (2)									
ϵ_0									
0.0000	9.19 (0)	8.51 (0)	8.07 (0)	7.98 (0)	0.5624	18.7 (8)	17.8 (9)	17.0 (8)	16.2 (7)
0.0869	9.6 (3)	9.1 (1)	8.8 (2)	8.4 (6)	0.6666	20.01 (0)	19.1 (1)	18.2 (2)	17.1 (6)
0.1764	10.7 (4)	10.2 (5)	9.8 (5)	9.5 (6)	0.7742	20.7 (9)	19.8 (2)	18.7 (9)	17.5 (7)
0.2686	12.4 (5)	11.8 (8)	11.4 (7)	11.0 (7)	0.8852	21.3 (1)	20.2 (5)	19.2 (3)	17.8 (7)
0.3636	14.4 (8)	13.7 (5)	13.2 (2)	12.7 (7)	1.0000	21.97 (0)	20.73 (0)	19.65 (0)	18.09 (0)
0.4615	16.7 (6)	15.8 (6)	15.2 (9)	14.6 (4)					
τ (ps)									
0.0000	6.15 (0)	5.71 (0)	5.6 (0)	5.26 (0)	0.5624	191.5 (1)	160.4 (4)	131.5 (2)	103.6 (3)
0.0869	13.4 (3)	12.1 (5)	11.5 (5)	10.5 (7)	0.6666	227.6 (7)	192.7 (3)	157.7 (4)	123.9 (3)
0.1764	24.4 (5)	22.6 (6)	22.4 (6)	21.0 (7)	0.7742	264.4 (7)	223.5 (3)	180.2 (3)	141.5 (1)
0.2686	54.5 (1)	49.3 (6)	44.5 (4)	41.4 (7)	0.8852	298.6 (3)	250.3 (2)	199.7 (3)	161.8 (3)
0.3636	102.4 (1)	86.8 (6)	73.5 (3)	62.6 (2)	1.0000	330.82 (0)	272.61 (0)	215.73 (0)	178.77 (0)
0.4615	148.3 (5)	126.1 (1)	104.4 (2)	84.5 (1)					
g^{eff}									
0.0000	0.68	0.64	0.61	0.62	0.5624	1.67	1.64	1.60	1.57
0.0869	0.73	0.70	0.69	0.68	0.6666	1.80	1.77	1.74	1.68
0.1764	0.84	0.82	0.81	0.80	0.7742	1.89	1.86	1.81	1.73
0.2686	1.02	1.00	0.99	0.97	0.8852	1.95	1.91	1.86	1.77
0.3636	1.23	1.19	1.18	1.17	1.0000	2.03	1.97	1.92	1.81
0.4615	1.46	1.42	1.41	1.38					

[a] x_1 is the mole fraction of propan-1-ol in the mixture. The numbers in parentheses indicate the error in the values (e.g., 41.4 (7) means 41.4 ± 7).

used. The reflected pulse without sample $R_l(t)$ and with sample $R_x(t)$ were digitized into 1024 points in the memory of the oscilloscope and transferred to a PC.

The temperature of the apparatus was controlled in a water bath and maintained at a constant temperature with an accuracy limit of ± 1 K by circulating water from a temperature controller through an insulated container in which the apparatus was suspended. The temperature of the apparatus was determined with an electronic thermometer.

Data Analysis

The time-dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$ over the frequency range (0.1 to 20) GHz using Fourier transformation[17,18] of

$$\rho^*(\omega) = (c/I\omega d)[p(\omega)/q(\omega)] \qquad (2)$$

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; d is the effective pin length; and $I = \sqrt{-1}$.

The complex permittivity spectra $\epsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying bilinear calibration method.[14] For the calibration process, propan-1-ol and respective chlorine molecules with propan-1-ol were used as calibrating liquids.

The experimental values of ϵ^* were fitted with the Havriliak−Nagami expression:[19−21]

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)}{[1 + (j\omega\tau)^{(1-\alpha)}]^\beta} \qquad (3)$$

with ϵ_0 and τ as adjustable parameters. A nonlinear least-squares fit method[22] was used to determine the values of dielectric parameters. The value of ϵ_∞ is taken to be fixed as 2.0. The parameter ϵ_∞ has not been used as a fitting parameter, as the data are not found to be sensitive with respect to this parameter. This is due to the fact that the upper frequency limit for $\epsilon^*(\omega)$ is 20 GHz. A sample $\rho^*(\omega)$ and $\epsilon^*(\omega)$ spectrum are shown in Figure 1a,b. This corresponds to 50 % propan-1-ol and 50 % dimethylene chloride mixture at 298 K.

Results and Discussion

The density and ϵ_0 values of pure liquid used are given in Table 1. The static dielectric constant (ϵ_0) and relaxation time (τ) obtained by fitting experimental data with the Havriliak−Negami equation are listed in Table 2 for PR + CB, PR + DE, and PR + DC systems, respectively. The values of α and β are taken to be 0 and 1 for the systems and are therefore not listed in Table 2. The dielectric constant and relaxation time values decrease with a decrease in the percentage of propan-1-ol in all the systems and decrease with an increase in temperature, as expected.

The Kirkwood correlation factor g is also a parameter for getting information regarding orientation of electric dipoles in polar liquids.[23] The g for pure liquid may be obtained by the expression

$$\frac{4\Pi N\mu^2\rho}{9kTM}g = \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} \qquad (4)$$

where μ is the dipole moment in gas phase, ρ is the density at temperature T, M is the molecular weight, k is the Boltzman constant, and N is Avogadro's number. The dipole moments for PR, CB, DE, and DC are taken as 1.69, 1.68, 2.06, and 1.60, respectively.[24]

For the mixture of two polar liquids 1 and 2, eq 4 is modified by ref 25 with the following assumptions:

Assume that, for the mixture, g^{eff} is the effective correlation factor in the mixture. The Kirkwood equation for the mixture may be expressed as

$$\frac{4\Pi N}{9kT}\left(\frac{\mu_1^2\rho_1}{M_1}\phi_1 + \frac{\mu_2^2\rho_2}{M_2}\phi_2\right)g^{\mathrm{eff}} = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(2\epsilon_{0m} + \epsilon_{\infty m})}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2} \qquad (5)$$

with ϕ_1 and ϕ_2 as volume fractions of liquids 1 and 2, respectively. The Kirkwood correlation factors (g^{eff}), which gives angular correlation between the molecules of the systems, are also tabulated in Table 2. The value of g^{eff} decreases, for all the systems, as the percent of propan-1-ol in the chlorine molecules decreases. The value of g^{eff} for chlorine molecules is less than 1, indicating antiparallel orientation of the electric dipole.

Conclusion

Dielectric relaxation parameters and Kirkwood correlation factor are reported in the paper for propan-1-ol with chlorine molecules at various concentrations and temperatures. The dielectric constant and relaxation time decrease with an increase in the percent of chlorine molecule. The interaction of the chlorine molecule on the hydrogen-bonded liquid propan-1-ol is discussed. The DC molecules interact with propan-1-ol in such a way that effective polarization gets enhanced, whereas they get reduced in the other two systems.

Acknowledgment

The author is thankful to Prof. S. C. Mehrotra, Department of Computer Science & IT, Dr. B.A.M. University, Aurangabad, for his valuable guidance.

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Received for review August 21, 2005. Accepted February 23, 2006. The financial assistance from the Department of Science and Technology is gratefully acknowledged.

JE0503397