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Static Dielectric Constant and Relaxation Time Measurements on Binary Mixtures of Dimethyl Sulfoxide with Ethanol, 2-Ethoxyethanol, and Propan-1-ol at 293, 303, 313, and 323 K

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Time domain spectroscopy in reflection mode has been used to determine complex reflection coefficient for 2-ethoxyethanol−dimethyl sulfoxide (DMSO), ethanol−DMSO, and propan-1-ol−DMSO mixtures at 293, 303, 313, and 323 K, in the frequency range of 10 MHz to 10 GHz. Further Fourier transform and least-squares fit methods have been used to obtain the complex permittivity, static dielectric constant, and relaxation time.

Introduction

The present paper reports the values of dielectric constants and relaxation times for binary mixtures of dimethyl sulfoxide (DMSO) with ethanol, 2-ethoxyethanol, and propan-1-ol at 293, 303, 313, and 323 K. The time domain reflectometry (Kumbharkhane et al., 1992, 1993; Puranik et al., 1991a,b, 1992; Hosamani et al., 1995) in reflection mode has been used to obtain the dielectric parameters.

Experimental Section

DMSO (AR grade), ethanol (Spectroscopy grade), propan-1-ol (AR grade), and 2-ethoxyethanol (Merck grade) were used without further purification. The solutions were prepared at 11 different volume percentages of 2-ethoxyethanol, ethanol, and propan-1-ol in DMSO from 0% to 100% in steps of 10% within 0.02% error limit. Using these volume percents, the mole fraction is calculated as

$$x = (m_1 v_1/\rho_1)/[(m_1 v_1/\rho_1) + (m_2 v_2/\rho_2)]$$

where m, v, and ρ represent the molecular weight, volume percentage, and density of the liquids, respectively. Subscripts 1 and 2 represent liquids 1 and 2, respectively.

The complex permittivity spectra were studied using the time domain reflectometry (TDR) (Cole et al., 1989; Puranik et al., 1991a,b) method. The Tektronix 7854 sampling oscilloscope with a 7S12 TDR unit has been used. A fast-rising step voltage pulse of 25 ps rise time generated by a tunnel diode was propagated through a coaxial line system. The sample was placed at the end of coaxial line in 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 condition. The change in the pulse after reflection from the sample placed in the cell was monitored by the sampling oscilloscope. In this experiment, a time window of 5 ns was used. The reflected pulses without sample $R_1(t)$ and with sample $R_x(t)$ were digitized in 1024 points and transferred to computer through GPIB (general purpose interface bus).

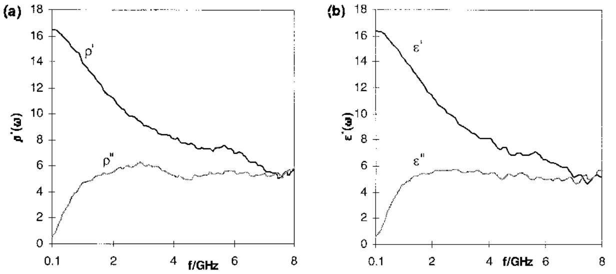

Figure 1. (a) $\rho^*(\omega)$ spectra of 2-ethoxyethanol at 293. K. (b) $\epsilon^*(\omega)$ spectra of 2-ethoxyethanol at 293. K.

Table 1. Comparison of Data for the Liquids Used with Literature Values at 293 K

	ϵ_0		ρ (g/cm^3)	
liquids	this work	lit.	this work	lit.
ethanol	25.71	25.43[b]	0.7893	0.7893[a]
propan-1-ol	20.05	20.45[b]	0.8035	0.8035[a]
2-ethoxyethanol	16.98		0.9297	0.9297[a]
DMSO	48.17	46.48[c] (at 298.15 K)	1.1014	1.1014[a]

[a] Weast, 1970−1. [b] National Academy of Sciences, 1976. [c] Barthel et al., 1990.

The temperature controller system with water bath and a thermostat has been used to maintain constant temperature within an accuracy of ±1 K. The sample cell is surrounded by a heat insulating container through which the water of constant temperature from the temperature controller system is circulated.

Results and Discussion

The time dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$ over the frequency range from 10 MHz to 10 GHz using Fourier transformation (Shannon, 1949; Samulon, 1951) as

$$\rho^*(\omega) = (c/j\omega d)[p(\omega)/q(\omega)] \tag{1}$$

where $p(\omega)$ and $q(\omega)$ are Fourier transforms of $(R_1(t)$ −

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Table 2. Dielectric Constant and Relaxation Time for 2-Ethoxyethanol (1)−DMSO (2), Ethanol (1)−DMSO (2), and Propan-1-ol (1)−DMSO (2) Mixtures[a]

x_2	ϵ_0	τ (ps)	ϵ_0	τ (ps)
(a) 2-Ethoxyethanol (1)−DMSO (2)				
	293. K		303. K	
0.0	16.98(11)	48.13(83)	16.45(13)	40.43(82)
0.0752	20.16(17)	54.50(111)	19.54(13)	42.79(75)
0.1547	20.55(20)	57.89(134)	20.34(16)	43.90(88)
0.2387	27.84(22)	52.55(98)	26.09(20)	41.73(83)
0.3279	30.89(24)	47.26(90)	29.97(28)	39.97(94)
0.4226	35.03(22)	41.37(65)	34.09(22)	35.24(62)
0.5233	37.05(16)	39.23(43)	35.56(22)	33.47(56)
0.6307	42.60(19)	30.62(38)	40.96(12)	29.36(25)
0.7454	44.13(13)	27.30(25)	46.03(30)	26.32(53)
0.8682	47.61(61)	27.73(97)	46.61(16)	22.63(27)
1.00	48.17(22)	23.02(34)	46.95(25)	20.09(37)
	313. K		323. K	
0.0	15.89(12)	36.66(71)	13.98(12)	27.22(78)
0.0752	19.32(13)	37.10(72)	18.78(14)	34.43(77)
0.1547	20.31(14)	36.28(71)	19.57(13)	34.65(69)
0.2387	26.83(17)	35.52(62)	25.25(16)	35.40(62)
0.3279	32.64(10)	33.68(28)	30.24(17)	32.38(52)
0.4226	35.44(12)	31.46(31)	33.71(18)	29.36(46)
0.5233	37.04(13)	28.53(30)	37.69(13)	26.94(29)
0.6307	40.77(18)	25.05(36)	39.15(19)	24.12(39)
0.7454	45.21(14)	22.93(24)	41.85(18)	22.53(33)
0.8682	45.43(54)	22.02(79)	42.14(13)	20.58(21)
1.00	44.95(24)	15.44(35)	43.30(34)	14.91(50)
(b) Ethanol (1)−DMSO (2)				
	293. K		303. K	
0.0	25.71	130.69	23.42	90.10
0.1448	31.05(4)	91.66(31)	28.49(13)	75.38(13)
0.2758	34.40(10)	70.27(55)	30.83(2)	61.96(12)
0.3950	36.48(7)	58.62(32)	34.85(3)	50.43(16)
0.5038	39.05(10)	51.92(40)	37.47(3)	42.42(13)
0.6037	42.53(6)	44.94(22)	39.14(16)	38.15(56)
0.6956	43.86(19)	40.21(59)	41.66(19)	34.34(61)
0.7804	46.39(23)	34.83(64)	45.26(7)	29.76(20)
0.8590	49.38(9)	31.42(22)	47.75(4)	26.10(11)
0.9320	49.50(15)	26.94(37)	48.19(7)	23.32(19)
1.00	48.17	23.02	46.95	20.09
	313. K		323. K	
0.00	22.23	71.78	20.43	53.77
0.1448	27.52(4)	56.12(24)	25.84(3)	50.58(18)
0.2758	30.02(8)	49.48(41)	28.84(2)	42.02(11)
0.3950	32.81(5)	41.69(22)	31.52(5)	35.59(23)
0.5038	35.89(10)	36.24(37)	34.09(5)	31.45(20)
0.6037	38.74(10)	32.25(33)	37.76(4)	27.73(16)
0.6956	41.34(13)	29.16(40)	40.43(4)	25.76(13)
0.7804	43.02(10)	26.67(28)	43.19(7)	22.96(21)
0.8590	45.58(15)	23.24(40)	44.56(4)	23.03(12)
0.9320	46.73(11)	19.17(29)	45.23(11)	18.47(28)
1.00	44.95	15.44	43.30	14.91
(c) Propan-1-ol (1)−DMSO (2)				
	293. K		303. K	
0.00	20.05	267.45	18.96	133.85
0.0953	22.94(3)	170.35(58)	21.93(4)	107.19(48)
0.1916	25.95(6)	106.02(63)	24.39(5)	77.67(48)
0.2980	29.21(7)	83.66(51)	27.53(5)	63.09(32)
0.2873	33.15(6)	65.61(35)	31.51(5)	48.67(28)
0.4876	36.77(8)	52.07(36)	34.87(7)	41.46(29)
0.5872	40.68(5)	44.29(20)	38.79(8)	34.12(27)
0.6887	47.04(47)	37.39(34)	42.07(9)	29.62(29)
0.7914	46.72(13)	31.84(37)	44.45(6)	26.50(18)
0.8951	54.10(72)	25.53(59)	47.11(10)	23.63(26)
1.00	48.17	23.02	46.95	20.09
	313. K		323. K	
0.00	17.37	86.66	15.92	79.78
0.0953	21.02(2)	80.04(26)	19.98(3)	70.42(35)
0.1916	23.63(4)	62.92(32)	23.52(3)	51.95(22)
0.2890	26.73(3)	50.44(21)	26.69(3)	40.67(17)
0.3873	30.50(3)	42.08(17)	30.55(5)	35.08(22)
0.4876	34.27(4)	35.22(16)	34.18(4)	30.79(16)
0.5872	36.93(3)	30.19(10)	37.67(5)	27.74(16)
0.6887	41.29(8)	26.19(24)	41.20(9)	23.58(26)
0.7914	44.01(5)	23.84(15)	43.63(4)	21.96(13)
0.8951	46.83(6)	20.42(14)	46.08(9)	19.02(24)
1.00	44.95	15.44	43.30	14.91

[a] Values in parentheses represent errors, e.g., 16.98(11) means 16.98 ± 0.11.

$R_x(t)$) 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 $j = \sqrt{-1}$.

The complex permittivity spectra $\epsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying a bilinear calibration method (Cole et al., 1989). For the calibration process, DMSO and the respective liquid mixed with DMSO were used as calibrating liquids. The examples of $\rho^*(\omega)$ and $\epsilon^*(\omega)$ spectra are shown in Figure 1a,b, respectively. This corresponds to the 2-ethoxyethanol at 293 K.

The experimental values of ϵ^* are fitted with the Debye expression

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{[1 + j\omega\tau]} \qquad (2)$$

with ϵ_0 and τ as fitting parameters. A least-squares fit method (Bevington, 1969) was used to determine the values of dielectric parameters. 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 10 GHz.

Table 1 gives the values of static dielectric constant and density of the pure liquids used along with literature values. The static dielectric constant and relaxation time obtained by fitting experimental data are listed in Table 2.

Conclusion

Dielectric relaxation parameters have been determined for 2-ethoxyethanol−DMSO, ethanol−DMSO, and propan-1-ol−DMSO mixture systems at 293, 303, 313, and 323 K. The measurements have been done at 11 values of concentrations, as shown in Table 2. These data provide information regarding solute−solvent interactions in liquids.

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