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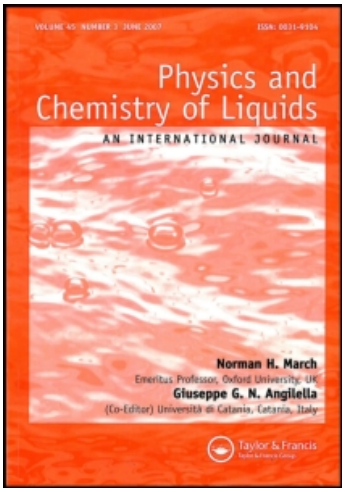

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DENSITIES, ADIABATIC COMPRESSIBILITY, FREE-LENGTH, VISCOSITIES AND EXCESS VOLUMES OF P-CRESOL(1) + DIMETHYL SULFOXIDE (2), + DIMETHYL FORMAMIDE (2), AND + 1,4-DIOXANE AT 303.15-318.15 K

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Measurements of density, ultrasonic velocity and viscosities for binary mixtures of p-cresol (1) with dimethyl sulfoxide (2) dimethyl formamide (2) and 1,4-dioxane (2) mixtures are reported at 303.15– 318.15 K over the entire range of composition. Also, the other related physical parameters, viz. adiabatic compressibility, intermolecular freelength, excess volume, excess adiabatic compressibility and excess viscosity, have been computed. The extent and nature of interaction among the component liquids are discussed.

KEY WORDS: Molefraction, density, compressibility, viscosity and excess volume.

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INTRODUCTION

A knowledge of densities, excess volumes and viscosities of fluids and fluid mixtures is essential to understand the molecular interactions between unlike molecules, to develop new theoretical models and also for engineering applications in the process industry. Ultrasonic methods find extensive applications owing to their ability of characterizing the physico-chemical behaviour of liquid systems from absorption and velocity data. The variation of these properties with temperature and composition for mixtures containing polar and hydrogen bonded components may be complex due to a decrease and/or an increase in hydrogen-bonding interaction due to mixing. Considerable work[1,2] has been reported on p-cresol as one of the component. We report new experimental data for the binary liquid mixtures of p-cresol(1) + Dimethylsulfoxide(2), + dimethylformamide(2) and + 1,4-dioxane(2) at 303.15 to 318.15 K. Further the data have been obtained at a range of temperatures with a view to understand the effect of temperature on these properties.

EXPERIMENTAL

Densities of liquids and liquid mixtures were measured by using a bicapillay pycnometer[3] at 303.15 to 318.15 K. The pycnometer was calibrated with deionized

double -distilled water. Density values are reproducible to $\pm 5 \times 10^{-5}$ g.c.[3]. Excess volumes were computed from density and comparities with the equation

$$V^E = [XM_1 + (1-X)M_2]/\rho_m - XM_1/\rho_1 - (1-X)M_2/\rho_2 \tag{1}$$

where X are the molefraction of p-cresol, M_1, M_2 represent molecular masses and ρ_m, ρ_1, ρ_2 are the densities of the mixture, component 1 and component 2 respectively.

Ultrasonic velocities were measured with a single-crystal ultrasonic interferometer at a frequency of 2MHz and these are acurate to ± 0.02. The measurements were made at 303.15, 308.15, 313.15 and 318.15 K. The temperature was maintained by circulating water around the liquid cell from a Ul0 thermostat controlled to ± 0.0l K. Adiabatic compressibilities were calculated from the relation

$$\beta_{ad} = \frac{1}{u^2 \rho} \tag{2}$$

where u is the ultrasonic velocity. Deviations in excess adiabatic compressibility were obtained using the equation.

$$\beta_{ad}^E = \beta_{ad} - [\beta_{ad_1} x + \beta_{ad_2}(1-x)] \tag{3}$$

where β_{ad}, β_{ad_1} and β_{ad_2} are the adiabatic compressibilities of the mixture and the pure components respectively.

Intermolecular free length (Lf) has been evaluated by Jacobson's formula[4, 5]

$$Lf = K(\beta_{ad})^{1/2} \tag{4}$$

where K is Jacobson's constant which is temperature dependent[5] but independent of the nature of the liquid. Rao's constant[6] has been calculated using the formula

$$R = -\frac{\bar{M}}{\rho} \cdot C\,1/3$$

where $\bar{M} = x_1 M_1 + x_2 M_2$ which is the mean molecular weight.

$$\therefore R = \bar{V} \cdot c\,1/3 \tag{5}$$

where $\bar{M}/\rho = \bar{V}$, ie the mean molar volume

Wada's constant[7] has been calculated using the formula

$$W = \bar{V} \cdot (\beta ad)^{-1/7} \tag{6}$$

Viscosities were measured using a Ostawald viscometer. The viscometer was calibrated at each temperature using distilled water. The viscometer constant, K, was calculated from the viscosity, η_w, density, ρ_w, and flow time, tw of water using the relation $K = \eta_w/\rho_w$, tw. The K values tabulated in Table 1 are the average of 10

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measurements and these measurements did not differ more than $\pm 0.0005\,cm^2 \cdot s^{-2}$. An electronic stop watch capable of measuring time to ± 0.015 was used for the time measurement. Kinetic energy corrections were negligible. The estimated error in viscosity was $\pm 5 + 10^{-4}$ cp. The performance of the viscometer was assessed by measuring and comparing the viscosities of the pure component with the values reported in the literature. Experimental viscosity values were used to calculate η^E using the relations[8].

$$\eta^E = \eta_m - \sum x_i \eta_i \tag{7}$$

where η is the viscosity, superscript E stands for excess and subscripts i and m stand for pure components and the mixture respectively.

The liquids p-cresol, dimethylformamide and 1, 4-dioxane used were of AR (BDH) grade and were distilled and purified by standard methods described by Weissberger[9]. Dimethyl sulfoxide was purified by the method described by Gopal *et al*[10]. Their purities were checked by measuring densities and comparing the data with those reported in literature[11, 12]. Solvent mixtures were prepared on Wt/Wt basis and the mole fractions (x) were calculated from the weights and densities of individual components[13].

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RESULTS AND DISCUSSION

The experimental densities (ρ) ultrasonic velocity (u), viscosities and the derived adiabatic compressibility (βad), mean molecular weight($\bar{M}$), mean molar volume ($\bar{V}$) and intermolecular freelength (Lf) at 303.15–318.15 K over the range of composition for the three systems are included in Table 1. The computed values of excess volumes, excess compressibility, excess viscosity, Rao's constant and Wada's constant at 303.15– 318.15 K for the three systems are given in Table 2. The variation of velocity with the mole fraction of p-cresol at four different temperatures for the three systems is represented in Figures 1–3 respectively. The Figures 1–2 indicate the velocity reaches a broad maximum for all the temperatures studied, where as Figure 3 shows that the velocity increases non linearly with an increasing trend at all temperatures. The variation of adiabatic compressibility (βad) with the molefraction of p-cresol at four temperatures for the three systems in Table 1 indicates that the system p-cresol(1) + dimethyl sulfoxide(2) show a broad minimum at about 0.2 mole fraction for all temperatures, where as p-cresol(1) + Dimethylformamide(2) and + 1, 4-dioxane(2) indicate that the compressibility decreases non linearly with the molefraction for all temperatures.

The variation of mean free length with molefraction at the four temperatures for the systems studied is shown in Figures 4–6 respectively. The curve 4 show a broad minima at about 0.2 molefraction for all the temperatures where as curves 5–6 indicates that mean free length non-linearily decreases without exhibiting any minima.

The variation of viscosity with the molefraction of p-cresol for the three systems in Table 1. indicates that the viscosity increases regularly without having any maxima. Same trend is seen at all the temperatures.

Table 1 Ultrasonic velocity (u), density (ρ), viscosity (η), adiabatic compressibility (βad), Mean molecular weight, ($\bar{M}$), Mean molar volume ($\bar{V}$) and Intermolecular free lengths (Lf) at 303.15 K, 308.15 K, 313.15 K and 318.15 K respectively.

X	$U(ms^{-1})$	$\rho(g.cm^{-3})$	$\eta.C.P.$	$\beta_{ad} \times 10^{12}$ $(Cm^2/dyne)$	$\bar{M}(g)$	$\bar{V}(g)$ (Cm^3, mol^{-1})	$Lf A^\circ$
P-Cresol(1) + Dimethyl Sulfoxide(2) at 303.15 K							
0.0000	1469.6	1.0890	1.7290	42.51	78.13	71.74	0.4088
0.0702	1469.6	1.0840	2.0360	42.71	80.22	74.01	0.4097
0.1453	1473.0	1.0790	2.3070	42.71	82.49	76.45	0.4097
0.2257	1488.0	1.0740	2.9130	42.05	84.90	79.05	0.4066
0.3119	1484.0	1.0670	3.4560	42.55	87.49	81.99	0.4090
0.4047	1483.2	1.0610	4.2770	42.84	90.26	85.07	0.4104
0.5050	1484.8	1.0570	5.0560	42.91	93.28	88.25	0.4107
0.5778	1480.8	1.0490	6.5240	43.47	90.93	86.68	0.4134
0.7312	1485.6	1.0460	7.9079	43.40	100.07	95.85	0.4130
0.8595	1482.5	1.0350	9.4990	43.96	103.92	100.40	0.4157
1.0000	1471.2	1.0250	10.0700	45.07	108.14	105.50	0.4209
P-Cresol(1) + Dimethyl Sulfoxide at 308.15 K							
0.0000	1458.4	1.0870	1.5631	43.25	78.13	71.87	0.4123
0.7020	1440.8	1.0810	1.7920	44.56	80.22	74.21	0.4185
0.1453	1456.0	1.0750	2.0400	43.88	82.49	76.73	0.4153
0.2257	1473.6	1.0710	2.5650	42.98	84.90	79.27	0.4111
0.3119	1468.0	1.0650	3.0620	43.57	87.49	82.15	0.4138
0.4047	1469.6	1.0580	3.7090	43.76	90.26	85.31	0.4147
0.5050	1465.6	1.0530	4.3240	44.21	93.28	88.58	0.4169
0.5778	1474.4	1.0480	5.4030	43.89	90.93	86.76	0.4154
0.7312	1467.2	1.0400	6.5430	44.66	100.07	96.22	0.4190
0.8595	1457.6	1.0330	7.6550	45.56	103.92	100.60	0.4232
1.0000	1454.4	1.0240	7.7410	46.16	108.14	105.60	0.4260
P-Cresol (1) + Dimethyl sulfoxide at 313.15 K.							
0.0000	1440.8	1.0830	1.4484	44.47	78.13	72.14	0.4181
0.0702	1440.8	1.0770	1.6040	44.72	80.22	74.49	0.4193
0.1453	1455.2	1.0710	1.8330	44.09	82.49	77.02	0.4163
0.2257	1457.6	1.0670	2.2930	44.11	84.90	79.57	0.4164
0.3119	1455.2	1.0610	2.6980	44.50	87.49	82.46	0.4183
0.4047	1455.2	1.0550	3.2400	44.76	90.26	85.56	0.4194
0.5050	1452.0	1.0490	3.7690	45.21	93.28	88.92	0.4216
0.5718	1449.6	1.0430	4.6490	45.62	90.93	87.18	0.4235
0.7312	1456.0	1.0370	5.7450	45.48	100.07	96.50	0.4228
0.8595	1445.6	1.0280	6.0830	46.54	103.92	101.09	0.4277
1.0000	1433.6	1.0210	6.2160	47.65	108.14	105.91	0.4328
P-Cresol (1) + Dimethylsulfoxide (2) at 318.15 K							
0.0000	1418.4	1.0780	1.3424	46.10	78.13	72.47	0.4257
0.0702	1425.6	1.0720	1.4760	45.84	80.22	74.84	0.4247
0.1453	1440.8	1.0670	1.6680	45.14	82.49	77.31	0.4212
0.2257	1439.2	1.0640	2.0540	45.37	84.90	79.79	0.4223
0.3119	1438.4	1.0570	2.4170	45.72	87.49	82.77	0.4239
0.4049	1440.0	1.0510	2.8570	45.88	90.26	85.88	0.4247
0.5050	1433.6	1.0460	3.3280	46.51	93.28	89.18	0.4276
0.5778	1435.2	1.0410	4.0100	46.63	90.93	87.34	0.4281
0.7312	1435.2	1.0340	4.9450	46.95	100.07	76.78	0.4296
0.8595	1434.4	1.0260	5.1110	47.37	103.92	101.29	0.4315
1.0000	1419.2	1.0170	5.2920	48.81	108.14	106.33	0.4380

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Table 1 (*continued*)

P-Cresol (1) + Dimethyl formamide (2) at 303.15 K							
0.0000	1435.0	0.9391	0.733	51.71	74.09	78.89	0.4508
0.0758	1441.6	0.9400	0.908	51.18	76.67	81.56	0.4486
0.1553	1456.6	0.9580	1.098	49.19	79.34	82.81	0.4397
0.2404	1486.8	0.9680	1.444	46.73	82.27	84.99	0.4286
0.3298	1470.4	0.9790	1.832	47.24	85.31	87.14	0.4309
0.4247	1468.4	0.9900	2.452	46.84	88.54	89.43	0.4291
0.5255	1479.0	0.9990	3.351	45.76	91.98	92.07	0.4241
0.6327	1481.6	1.0080	4.534	45.19	95.63	94.87	0.4215
0.7472	1481.6	1.0150	6.256	44.88	99.53	98.06	0.4200
0.8692	1479.2	1.0210	7.994	14.76	103.68	101.55	0.4195
1.0000	1471.2	1.0250	10.070	45.07	108.14	105.50	0.2695
P-Cresol (1) + Dimethylformamide (2) at 308.15 K							
0.0000	1424.0	0.9362	0.719	52.67	74.09	79.13	0.4550
0.0758	1428.0	0.9460	0.787	51.83	76.67	81.04	0.4514
0.1553	1436.0	0.9550	0.988	50.77	79.34	83.07	0.4468
0.2404	1450.0	0.9620	1.208	49.15	82.27	85.08	0.4396
0.3298	1442.4	0.9767	1.611	49.21	85.31	87.34	0.4398
0.4247	1452.8	0.9872	2.165	47.99	88.54	89.69	0.4343
0.5155	1461.6	0.9960	2.886	46.99	91.98	92.35	0.4298
0.6327	1464.0	1.0050	3.905	46.42	95.63	95.15	0.4272
0.7472	1466.4	1.0120	5.298	45.95	99.53	98.35	0.4250
0.8692	1461.6	1.0180	6.386	45.98	103.68	101.85	0.4251
1.0000	1454.4	1.0240	7.741	46.16	108.14	105.60	0.4260
P-Cresol (1) + Dimethylformamide (2) at 313.15 K							
0.0000	1339.2	0.9318	0.640	54.81	74.09	79.51	0.4642
0.0758	1408.8	0.9430	0.769	53.43	76.67	81.30	0.4583
0.1553	1421.6	0.9500	0.913	52.08	79.34	83.51	0.4525
0.2405	1430.4	0.9670	1.284	50.54	82.27	85.08	0.4457
0.3298	1430.4	0.9730	1.465	50.23	85.31	87.67	0.4443
0.4247	1430.4	0.9830	1.952	49.72	88.54	90.07	0.4421
0.5256	1445.6	0.9930	2.562	48.18	91.98	92.63	0.4352
0.6327	1449.6	1.0010	3.375	47.54	95.63	95.53	0.4223
0.7472	1454.4	1.0090	4.489	46.85	99.53	98.65	0.4291
0.8692	1446.4	1.0140	5.777	47.13	103.68	102.25	0.4304
1.0000	1433.6	1.0210	6.216	47.65	108.14	105.91	0.4328
P-Cresol (1) + Dmethyl formamide (2) at 318.15 K							
0.0000	1390.4	0.9281	0.597	55.73	74.09	79.80	0.4680
0.0758	1391.2	0.9380	0.732	55.08	76.67	81.73	0.4653
0.1553	1404.8	0.9470	0.845	53.50	79.34	83.78	0.4586
0.2404	1409.6	0.9590	1.087	52.47	82.27	85.79	0.4542
0.3298	1417.6	0.9690	1.339	51.35	85.31	88.04	0.4493
0.4247	1419.2	0.9790	1.755	50.71	88.54	90.44	0.4465
0.5255	1429.6	0.9890	2.273	49.47	91.98	93.00	0.4410
0.6327	1436.0	0.9970	2.954	48.64	95.63	95.82	0.4372
0.7472	1436.0	1.0060	3.852	48.20	99.53	98.94	0.4353
0.8692	1434.4	1.0120	4.485	48.02	103.68	102.45	0.4345
1.0000	1419.2	1.0170	5.292	48.81	108.14	106.33	0.4380
P-Cresol (1) + 1,4-dioxane (2) at 303.15 K							
0.0000	1320.0	1.0188	1.0537	56.33	88.11	86.48	0.4706
0.0835	1342.4	1.0230	1.3351	54.24	89.78	87.76	0.4617

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Table 1 (*continued*)

X	$U(ms^{-1})$	$\rho(g.cm^{-3})$	$\eta.C.P.$	$\beta_{ad} \times 10^{12}$ $(Cm^2/dyne)$	$\bar{M}(g)$	$\bar{V}(g)$ (Cm^3, mol^{-1})	LfA°
0.1701	1358.4	1.0241	1.4758	52.91	91.51	89.36	0.4561
0.2600	1377.6	1.0239	1.7524	51.46	93.31	91.13	0.4498
0.3534	1394.4	1.0260	2.1645	50.12	95.18	92.77	0.4439
0.4504	1416.0	1.0279	2.7978	48.52	97.13	94.49	0.4367
0.5515	1433.6	1.0920	3.6505	44.55	99.15	90.80	0.4325
0.6567	1447.3	1.0288	4.7835	46.40	101.26	98.42	0.4271
0.7663	1460.0	1.0293	6.4128	45.57	103.45	100.51	0.4233
0.8807	1468.0	1.0280	8.2610	45.13	105.75	102.87	0.4212
1.0000	1471.2	1.0250	10.0700	45.07	108.14	105.50	0.4209
			P-Cresol (1) + 1,4-dioxane at 308.15 K				
0.0000	1302.4	1.0156	0.9469	58.04	88.11	86.75	0.4771
0.0835	1327.2	1.0185	1.1841	55.73	89.78	88.15	0.4653
0.1701	1338.4	1.0207	1.3195	54.69	91.51	89.66	0.4637
0.2600	1359.2	1.0220	1.5633	52.96	93.31	91.30	0.4563
0.3534	1378.2	1.0241	1.8871	51.40	95.18	92.94	0.4495
0.4505	1402.4	1.0259	2.4733	49.56	97.13	94.68	0.4414
0.5515	1417.6	1.0253	3.1082	48.53	99.15	96.70	0.4368
0.6567	1425.6	1.0269	4.0904	47.91	101.26	98.61	0.4340
0.7663	1444.0	1.0265	5.2758	46.72	103.45	100.78	0.4285
0.8807	1451.2	1.0218	5.7041	46.47	105.75	103.49	0.4274
1.0000	1454.4	1.0240	7.7410	46.16	108.14	105.60	0.4260
			P-Cresol (1) + 1,4-dioxane (2) at 313.15 K				
0.0000	1279.6	1.0106	0.8726	60.43	88.11	87.18	0.4874
0.0835	1308.0	1.0138	1.0972	57.65	89.78	88.56	0.4760
0.1701	1322.4	1.0165	1.2010	56.25	91.51	90.03	0.4702
0.2600	1340.0	1.0181	1.4218	54.70	93.31	91.65	0.4637
0.3534	1360.0	1.0202	1.7097	52.99	95.18	93.30	0.4564
0.4505	1384.0	1.0214	2.1746	51.11	97.13	95.09	0.4482
0.5515	1400.0	1.0228	2.7326	49.88	99.15	96.94	0.4428
0.6567	1413.6	1.0259	3.5239	48.78	101.26	98.70	0.4379
0.7663	1428.0	1.0231	4.4919	47.93	103.45	101.12	0.4340
0.8807	1430.6	1.0218	5.7041	47.81	105.75	103.49	0.4335
1.0000	1433.6	1.0210	6.2160	47.65	108.14	105.91	0.4328
			P-Cresol (1) + 1,4-dioxane (2) at 318.15 K				
0.0000	1264.8	1.0049	0.8128	61.20	88.11	87.68	0.4945
0.0835	1288.0	1.0077	0.9967	59.81	89.78	89.09	0.4849
0.1701	1305.6	1.0113	1.1058	58.00	91.51	90.49	0.4705
0.2600	1322.4	1.0131	1.2887	56.44	93.31	92.11	0.4710
0.3534	1344.8	1.0152	1.5418	54.46	95.18	93.76	0.4627
0.4505	1361.2	1.0171	1.9636	53.06	97.13	95.50	0.4567
0.5515	1381.6	1.0184	2.4087	51.44	99.15	97.36	0.4497
0.6567	1398.4	1.0183	3.6738	50.21	101.26	99.44	0.4443
0.7663	1411.2	1.0189	3.8043	49.28	103.45	101.53	0.4401
0.8807	1415.4	1.0178	4.8343	49.04	105.75	103.90	0.4390
1.0000	1419.2	1.0710	5.2920	48.81	108.14	106.33	0.4380

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Table 2 Excess volume, Excess compressibility, Excess viscosity, Rao's constant and Wada's constant at 303.15–318.15 K.

X	V^E cm^2/mol	$\beta^E_{ad} \times 10^{12}$ $cm^2/dyne$	η^E $C\,P$	*Rao's Constant*	*Wada's Constant*
		P-Cresol(1) + dimethyl sulfoxide (2) at 303.15 K			
0.000	0.0000	0.0000	0.0000	815.6	2174.8
0.0702	−0.0954	0.0209	−0.2784	841.4	2242.0
0.1453	−0.1989	−0.1753	−0.6339	869.8	2315.9
0.2257	−0.2405	−0.6028	−0.6986	902.5	2400.1
0.3119	−0.2774	−0.7588	−0.7846	935.2	2485.2
0.4047	−0.3218	−0.7049	−0.8274	970.2	2576.1
0.5050	−0.3878	−0.8961	−0.8852	1006.8	2671.7
0.5778	−0.3986	−0.9892	−0.8360	988.0	2619.3
0.7312	−0.5727	−0.9868	−0.6800	1093.7	2897.1
0.8595	−0.3502	−0.7482	−0.4309	1144.8	3029.1
1.0000	0.0000	0.0000	0.0000	1199.9	3171.5
		P-Cresol(1) + Dimethyl sulfoxide (2) at 308.15 K			
0.0000	0.0000	0.0000	0.0000	815.1	2173.4
0.0702	−0.0200	−0.2089	0.2046	838.2	2234.7
0.1453	−0.0422	−0.3637	−0.2997	869.7	2315.6
0.2257	−0.2145	−0.9124	−0.3925	902.1	2399.2
0.3119	−0.2464	−0.5908	−0.4280	933.6	2481.5
0.4047	−0.2008	−0.6641	−0.3541	970.0	2575.6
0.5050	−0.3199	−0.5125	−0.3589	1006.2	2670.4
0.5778	−0.3235	−0.8705	−0.3311	987.5	2618.2
0.7312	−0.3148	−0.7166	−0.2426	1093.4	2896.3
0.8595	−0.2629	−0.1935	−0.1420	1140.6	3019.6
1.0000	0.0000	0.0000	0.0000	1196.5	3163.8
		P-Cresol(1) + Dimethyl sulfoxide (2) at 313.15 K			
0.0000	0.0000	0.0000	0.0000	814.8	2172.8
0.0702	−0.0130	0.0292	−0.1789	841.3	2241.8
0.1453	−0.0276	−0.8488	−0.3081	872.8	2322.6
0.2257	−0.1930	−0.7845	−0.2314	902.2	2399.4
0.3119	−0.2161	−0.9624	−0.2374	934.4	2483.2
0.4047	−0.2418	−0.9996	0.2477	969.5	2574.6
0.5050	−0.2702	−0.8679	−0.0870	1006.9	2672.1
0.5778	−0.2835	−1.1959	−0.2100	986.6	2616.2
0.7312	−0.2247	−1.3141	−0.1505	1093.7	2897.2
0.8595	−0.0776	−0.6008	−0.9368	1143.0	3025.0
1.0000	0.0000	0.0000	0.0000	1194.2	3158.7
		P-Cresol(1) + Dimethyl sulfoxide (2) at 318.15 K			
0.0000	0.000	0.0000	0.0000	814.3	2171.7
0.0702	−0.0058	−0.3947	−0.1435	842.3	2243.9
0.1453	−0.0854	−1.3557	−0.1283	873.1	2323.0
0.2257	−0.1817	−1.3456	−0.1798	900.9	2396.5
0.3119	−0.2642	−1.2276	−0.2173	934.3	2488.3
0.4047	−0.2839	−1.3159	−0.2537	969.8	2575.3
0.5050	−0.3912	−0.9605	−0.2789	1005.6	2668.9
0.5778	−0.4785	−1.1803	−0.2635	985.2	2613.0
0.7312	−0.4493	−1.1386	−0.1947	1091.7	2892.5
0.8595	−0.2856	−1.0675	−0.1239	1141.3	3023.3
0.0000	0.0000	0.0000	0.0000	1194.9	3160.2

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Table 2 (*continued*)

X	V^E cm^2/mol	$\beta_{ad}^E \times 10^{12}$ $cm^2/dyne$	η^E CP	*Rao's Constant*	*Wada's Constant*
		P-Cresol (1) + dimethylformamide (2) at 303.15 K			
0.0000	0.0000	0.0000	0.0000	889.8	2325.6
0.0758	−0.6533	−0.0249	−0.5328	921.4	2407.7
0.1553	−0.4375	−0.9799	−1.0848	938.8	2458.7
0.2440	−0.5956	−2.2020	−1.5337	970.9	2541.9
0.3298	−0.6875	−2.2768	−1.9803	990.9	2602.0
0.4247	−0.7569	−2.3842	−2.2364	1016.5	2673.8
0.5155	−0.8937	−2.4598	−2.2886	1049.0	2761.9
0.6327	−0.8549	−2.3155	−2.1066	1081.5	2850.9
0.7472	−0.7078	−1.8668	−1.4537	1181.0	2949.8
0.8692	−0.4684	−0.8687	−0.8547	1157.1	3055.8
1.0000	0.0000	0.0000	0.0000	1198.4	3171.9
		P-Cresol (1) + dimethylformamide (2) at 308.15 K			
0.0000	0.0000	0.0000	0.0000	891.3	2326.6
0.0758	−0.0977	−0.3439	−0.4649	912.6	2388.2
0.1553	−0.1302	−0.8592	−0.8217	937.3	2455.2
0.2404	−0.4182	−1.9527	−1.1996	963.1	2526.2
0.3298	−0.5123	−1.3123	−1.4243	986.9	2593.0
0.4247	−0.6798	−1.9127	−1.5366	1015.8	2672.1
0.5255	−0.6945	−2.2570	−1.5234	1048.0	2759.7
0.6327	−0.7267	−2.1327	−1.2571	1080.5	2848.5
0.7472	−0.5634	−1.8646	−0.6681	1117.4	2948.6
0.8692	−0.2907	−1.0356	−0.4366	1155.8	3053.1
1.0000	0.0000	0.0000	0.0000	1196.5	3163.8
		P-Cresol (1) + dimethylformamide (2) at 313.15 K			
0.0000	0.0000	0.0000	0.0000	889.3	2324.3
0.0758	−0.2087	−0.8439	−0.2942	911.4	2385.4
0.1553	−0.0566	−1.5917	−0.5931	939.0	2459.3
0.2404	−0.7767	−2.5530	−0.6969	958.6	2516.2
0.3298	−0.5329	−2.2190	−1.0143	987.9	2595.3
0.4247	−0.6433	−2.7504	−1.0564	1014.9	2670.1
0.5255	−0.7558	−2.8643	−1.0085	1047.3	2758.1
0.6327	−0.6801	−2.7452	−0.7932	1081.2	2850.2
0.7472	−0.5973	−2.6185	−0.3176	1117.7	2949.2
0.8692	−0.2076	−1.4532	−0.2903	1156.4	3054.3
1.0000	0.0000	0.0000	0.0000	1194.2	3158.7
		P-Cresol (1) + dimethylformamide (2) at 318.15 K			
0.0000	0.0000	0.0000	0.0000	891.0	2328.1
0.0758	−0.0999	−0.1274	−0.2215	912.4	2387.7
0.1553	−0.1244	−1.1246	−0.4814	938.3	2457.6
0.2404	−0.4078	−1.5927	−0.6392	961.9	2523.6
0.3298	−0.5208	−2.0950	−0.8068	989.0	2597.8
0.4247	−0.6345	−2.0779	−0.8363	1016.3	2673.4
0.5255	−0.7505	−2.6269	−0.7916	1047.7	2758.9
0.6327	−0.6768	−2.4190	−0.6138	1082.1	2852.3
0.7472	−0.6946	−2.3680	−0.2533	1116.3	2946.0
0.8692	−0.4090	−1.6975	−0.1930	1155.4	3052.2

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Table 2 (*continued*)

1.0000	0.0000	0.0000	0.0000	1194.9	3160.2
		P-Cresol (1) + 1,4-dioxane (2) at 303.15 K			
0.0000	0.0000	0.0000	0.0000	948.7	2518.3
0.0835	−0.3082	−1.1478	−0.4715	968.1	2569.4
0.1701	−0.3557	−1.5001	−1.1116	989.7	2625.5
0.2600	−0.4393	−1.9427	−1.6455	1014.1	2688.3
0.3534	−0.4288	−2.2266	−2.0756	1036.4	2746.9
0.4505	−0.5548	−2.7409	−2.3177	1061.1	2810.9
0.5515	−0.5700	−5.5665	−2.3758	1023.8	2734.1
0.6567	−0.5445	−2.5360	−2.1912	1113.3	2946.6
0.7663	−0.5390	−2.1258	−1.5501	1140.3	3016.9
0.8807	−0.3635	−1.2785	−0.7334	1169.1	3091.7
1.0000	0.0000	0.0000	0.0000	1199.9	3171.5
		P-Cresol (1) + 1,4-dioxane (2) at 308.15 K			
0.0000	0.0000	0.0000	0.0000	947.4	2515.4
0.0835	−1.1788	−1.3161	−0.3301	968.7	2570.4
0.1701	−0.3017	−1.3344	−0.7831	988.1	2621.8
0.2600	−0.3483	−1.9948	−1.1501	1011.4	2682.3
0.3534	−0.4692	−2.4410	−1.4608	1034.3	2742.1
0.4505	−0.5667	−3.1334	−1.5343	1059.7	2807.9
0.5515	−0.6920	−2.9622	−1.5856	1086.4	2876.6
0.6567	−0.5236	−2.3303	−1.3182	1109.8	2938.6
0.7663	−0.4124	−2.2232	−1.1874	1139.2	3014.3
0.8807	0.2375	−1.1137	−1.2264	1171.7	3097.6
1.0000	0.0000	0.0000	0.0000	1196.5	3163.8
		P-Cresol (1) + 1,4-dioxane (2) at 313.15 K			
0.0000	0.0000	0.0000	0.0000	946.5	2513.4
0.0835	−0.1894	−1.7115	−0.2216	968.5	2570.2
0.1701	−0.3402	−2.0036	−0.5805	988.2	2622.1
0.2600	−0.3969	−2.4092	−0.8401	1010.5	2680.2
0.3534	−0.5011	−2.9222	−1.0513	1033.7	2740.7
0.4505	−0.5253	−3.5637	−1.1052	1059.7	2807.9
0.5515	−0.5692	−3.5033	−1.0859	1084.5	2872.4
0.6567	−0.7786	−3.2623	−0.8577	1107.7	2933.9
0.7663	−0.4155	−2.7100	−0.4755	1138.7	3013.3
0.8807	−0.1870	−1.3616	−0.1256	1166.1	3085.0
1.0000	0.0000	0.0000	0.0000	1194.2	3158.7
		P-Cresol (1) + 1,4-dioxane (2) at 318.15 K			
0.0000	0.0000	0.0000	0.0000	948.2	2517.2
0.0835	−0.1413	−1.2696	−0.1902	969.3	2572.2
0.1701	−0.3586	−1.9194	−0.4690	989.0	2624.0
0.2600	−0.4187	−2.2810	−0.6887	1011.0	2681.4
0.3534	−0.5086	−3.0082	−0.8540	1034.9	2743.4
0.4505	−0.5826	−3.1123	−0.8671	1058.3	2804.7
0.5515	−0.6019	−3.3814	−0.8744	1084.4	2872.2
0.6567	−0.4853	−3.1968	−0.7605	1112.0	2943.6
0.7663	−0.4335	−2.6655	−0.4409	1138.9	3013.7
0.8807	−0.2062	−1.3731	−0.0767	1166.5	3085.9
1.0000	0.000	0.0000	0.0000	1194.9	3160.2

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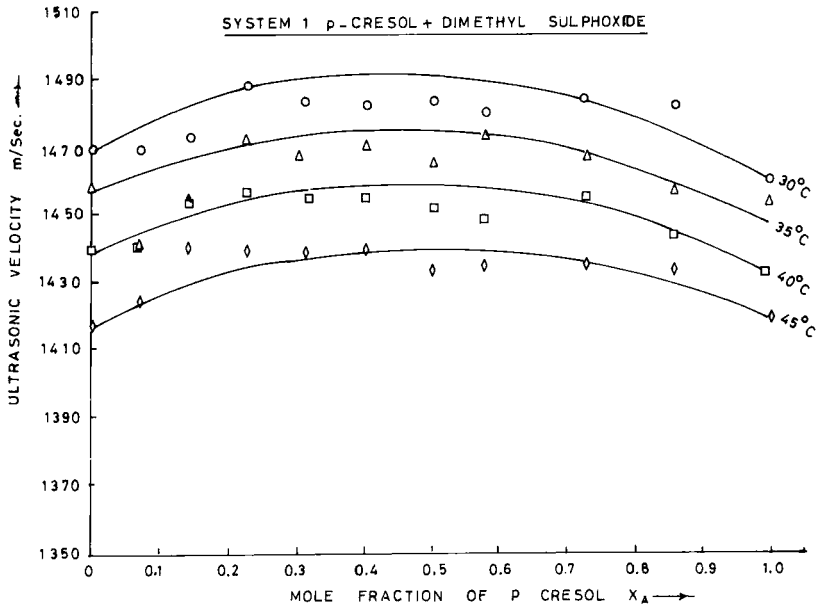

Figure 1 Variation of ultrasonic velocity with mole fraction of p-cresol.

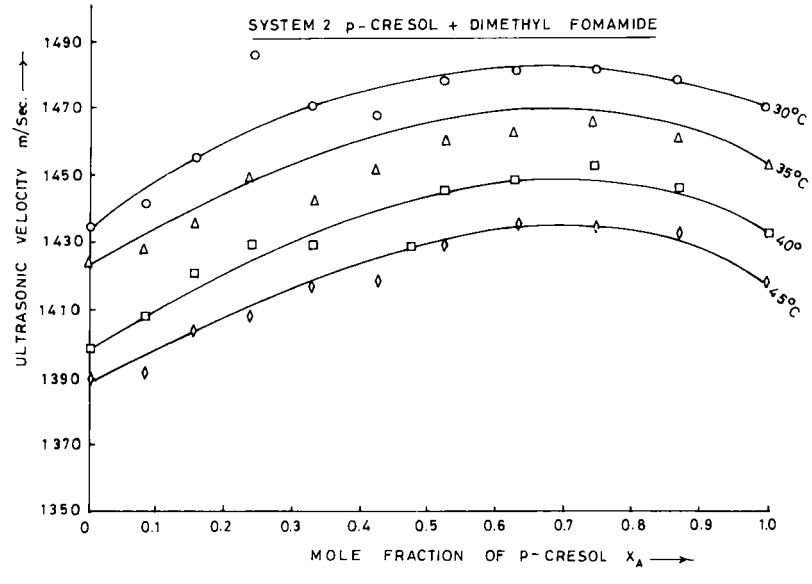

Figure 2 Variation of ultrasonic velocity with mole fraction of p-cresol.

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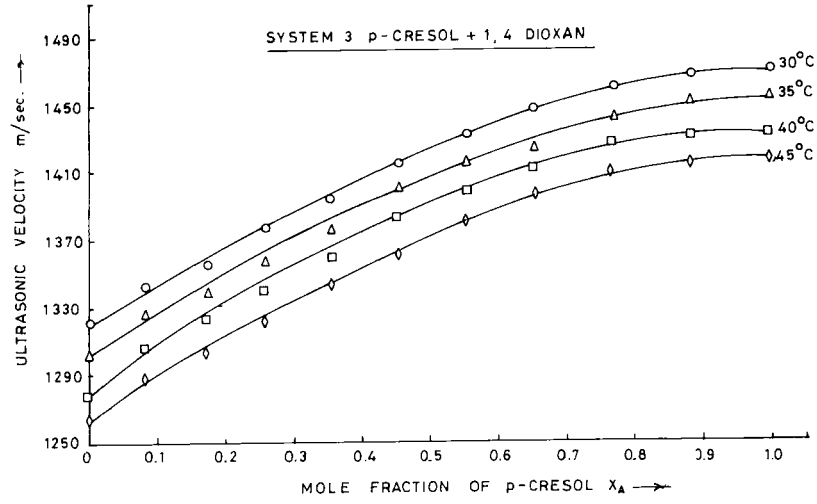

Figure 3 Variation of ultrasonic velocity with mole fraction of p-cresol.

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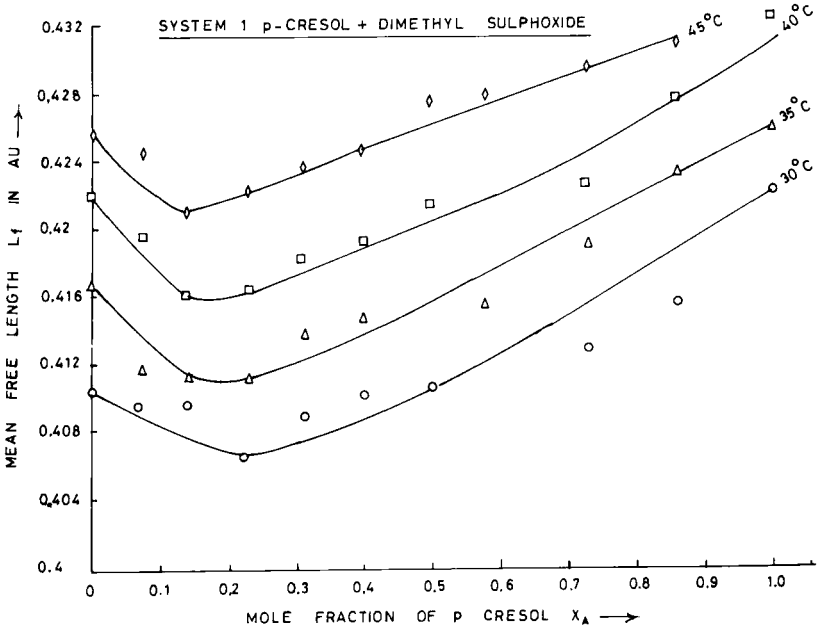

Figure 4 Variation of mean free length with mole fraction of p-cresol.

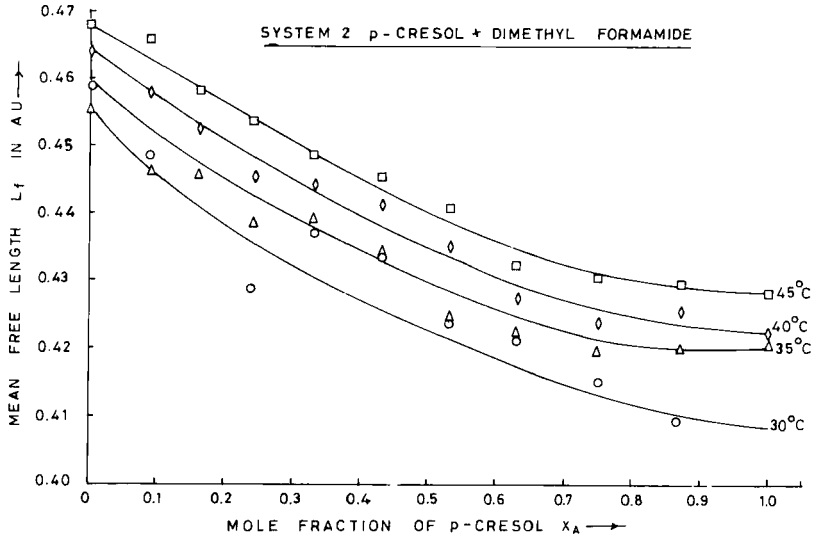

Figure 5 Variation of mean free length with mole fraction of p-cresol.

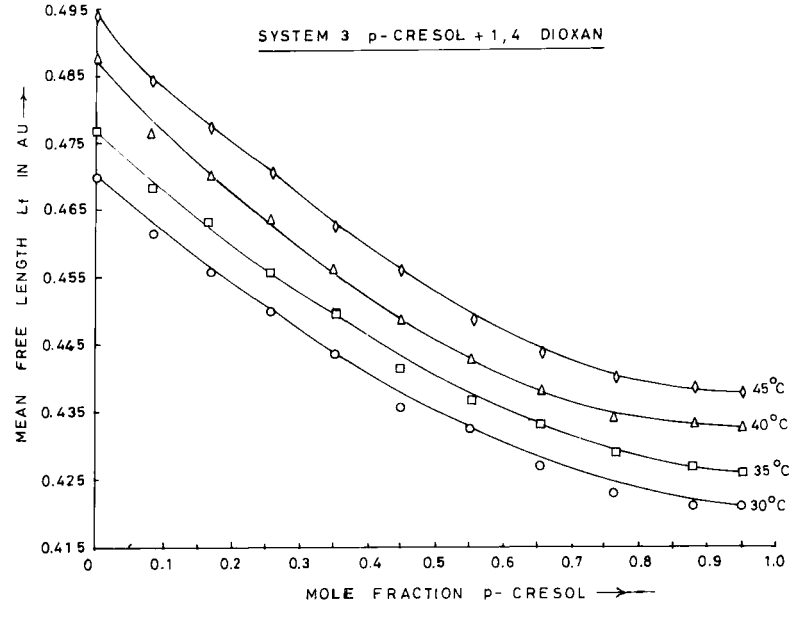

Figure 6 Variation of mean free lengthwith mole fraction of p-cresol.

The variation of excess volume with the molefraction at four different temperatures are shown in Figures 7–9 for the three systems respectively. While the variation of excess viscosity with the molefraction is shown in Figures 10–12 respectively. The Figures 7–12 indicates that the negative excess values reach abroad minimum at around 0.6 molefraction for all the temperatures studied in case of p-cresol(1) + dimethylformamide(2) and + 1, 4 dioxane(2) systems the excess

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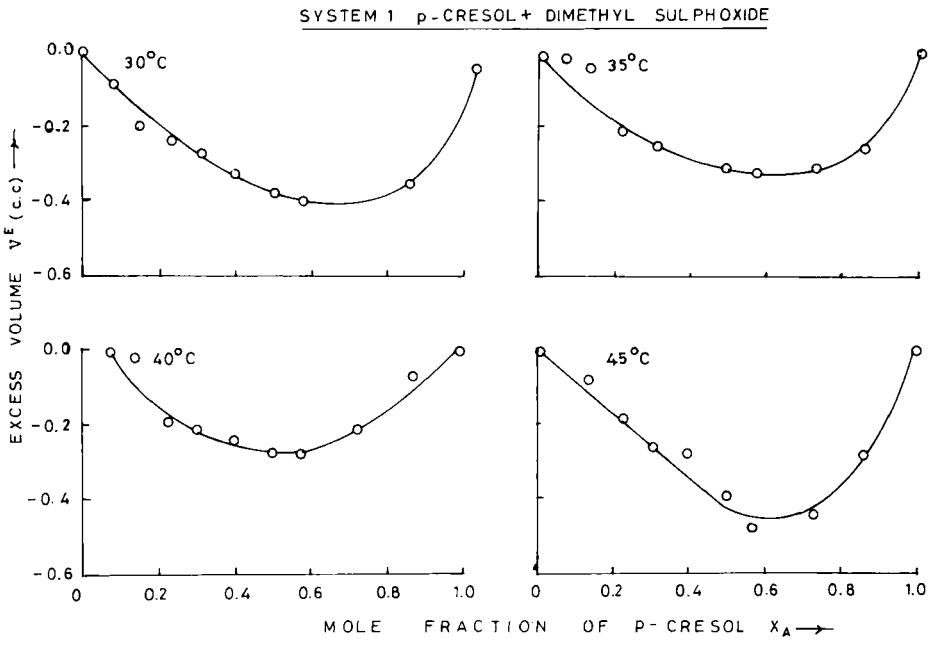

Figure 7 Variation of excess volume with mole fraction of p-cresol.

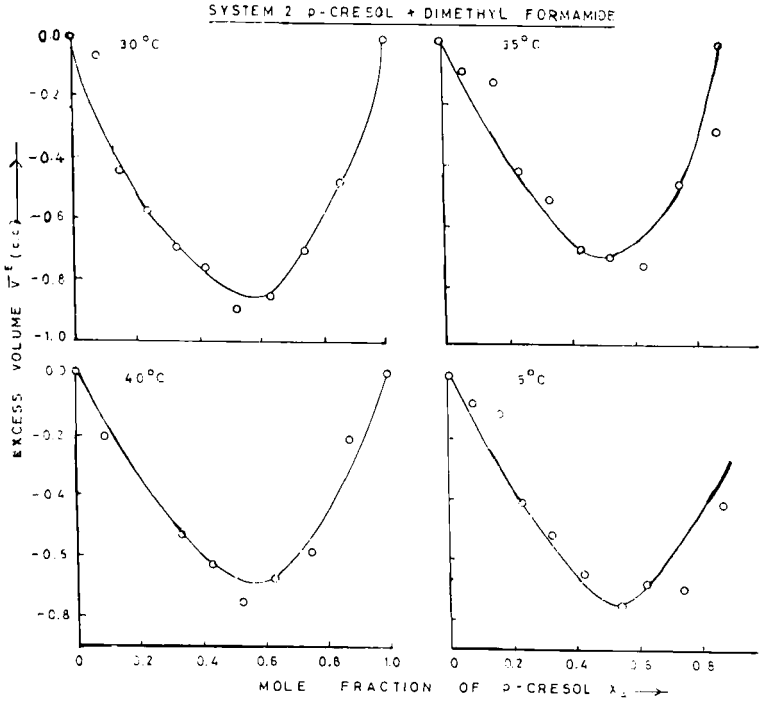

Figure 8 Variation of excess volume with mole fraction of p-cresol.

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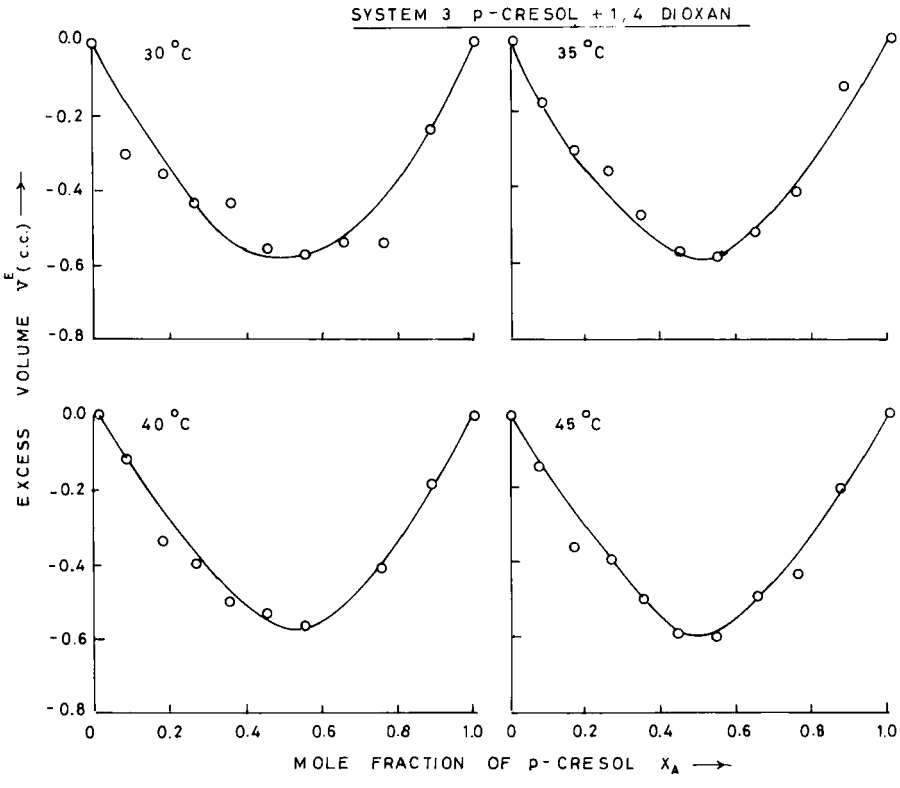

Figure 9 Variation of excess volume with mole fraction of p-cresol.

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negative properties show a minimum at around 0.5 molefraction and the excess values are found to decrease with increase in temperature.

The variation of Rao's constant and Wada's constant respectively with the mole fraction and temperature clearly indicates that there is a linearity of the constants in all the systems studied. Further, over the temperature range 303.15 K–318.15 K, the variation of these constants is almost negligible for any particular composition.

The similar trends have been reported earlier for non-aqueous hydrogen bonded binary liquid systems by several investigators[14–19]. The complex formation in the binary systems studied could be taking place through intermolecular hydrogen bond between the constituent liquids. The existance of structurally different species in solution is bound to have its effect reflected in the other physical parameters as well. In order to examine the possibility, excess volume of mixing in solution have been calculated both as a function of composition and temperatures. The data indicates that there exists a volume contraction in mixing. It is also understood that with increase in temperature, there is a down ward shift of the excess volume curves. The results suggest the close approach of unlike molecules due to hydrogen bonding.

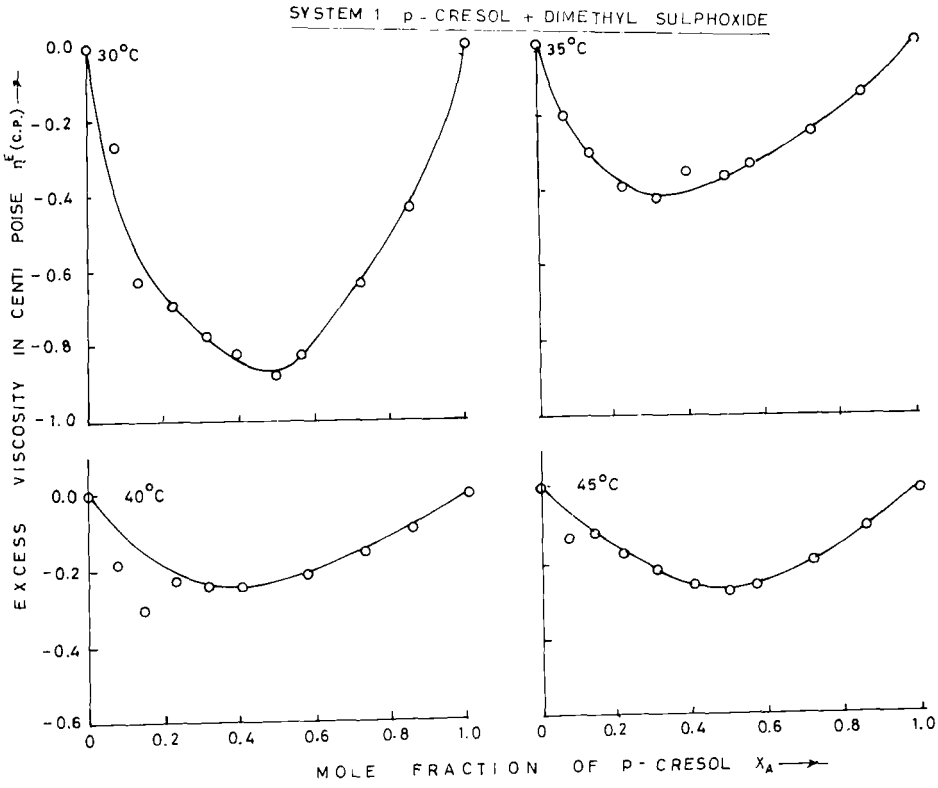

Figure 10 Variation of excess viscosity with mole fraction of p-cresol.

The minimum of mean free length also varies slightly with temperature. These results suggest that consequent on the formation of hydrogen bonded complexes in the solution, the free volume and hence free length are gradually reduced. The existence of a minimum in lf at a particular compositions in the p-cresol(l) + dimethylsulfoxide(2) systems might be an indication of the presence of molecular species with closer packing than either of constituent liquids. The closer packing of molecules due to the formation of hydrogen bonds and the corresponding structural changes in the mixture will have greater influence on the overall compressibility of the system. Deviations in adiabatic compressibility can be explained by the following factors.

1. Increase in free length due to loss of dipolar association difference in size and shape of the component molecules which lead to decrease in sound velocity and increase in adiabatic compressibility.
2. Decrease in free lengths as a result of dipole–dipole interactions or hydrogen bonded complex formation between unlike molecules which leads to increase of sound velocity and decrease of compressibility. The actual deviation depends on the dominant effect. The experimental values of negative excess compressibilities

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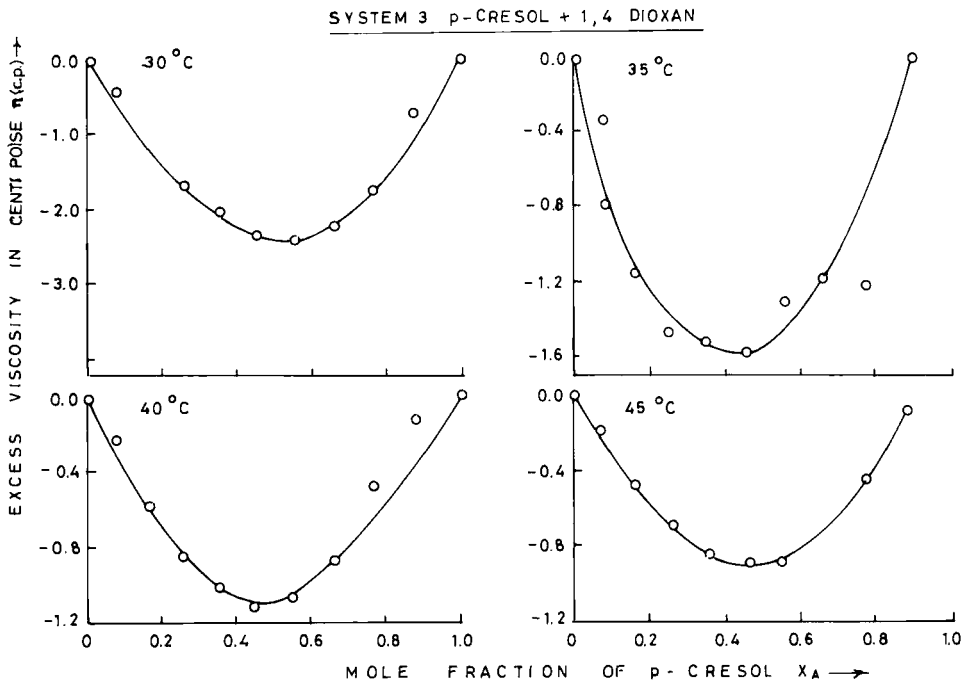

Figure 11 Variation of excess viscosity with mole fraction of p-cresol.

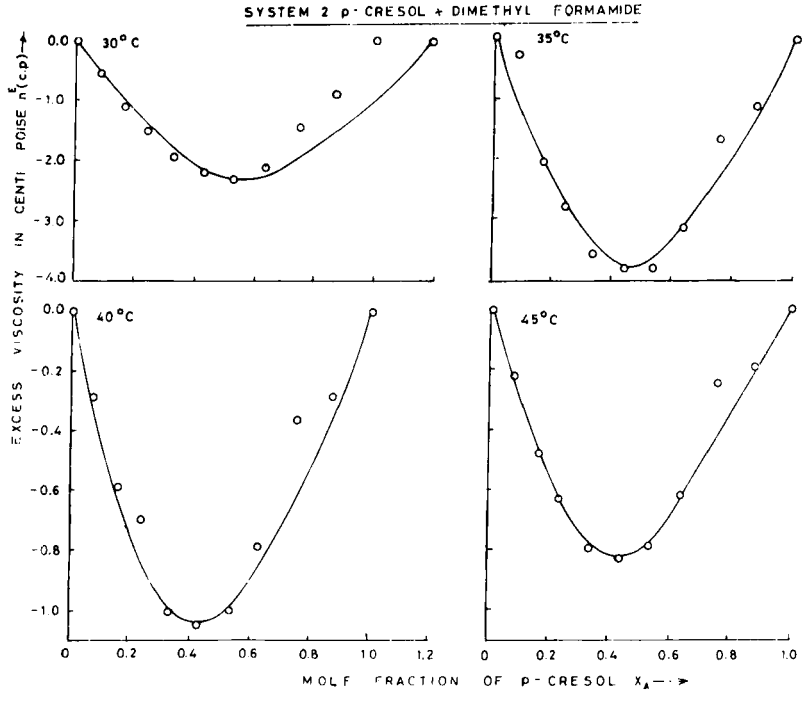

Figure 12 Variation of excess viscosity with mole fraction of p-cresol.

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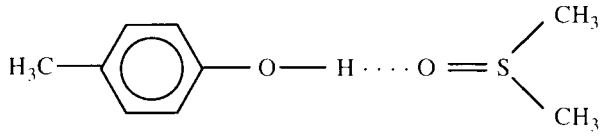
in all the three systems suggest that the hydrogen bond formation dominates the other contributions. The effect of temperature on the excess compressibilities is small for all the binary systems.

The excess viscosity variation gives a qualitative estimation of the strength of intermolecular interactions. The excess viscosities may be generally explained by considering the following factors.

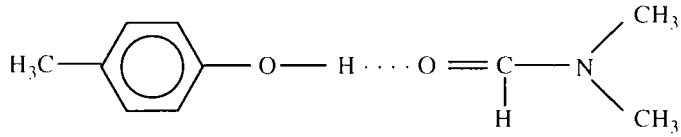
1. The difference in size and shape of the component molecules the loss of dipolar association in pure component may contribute to a decrease in viscosity and
2. Specific interactions between unlike components such as hydrogen bond formation and charge transfer complexes may cause for increase in viscosity in mixtures than in pure components. The former effect produces negative deviation in excess viscosity and latter effect produce positive deviation in excess viscosity. The excess viscosity is generally considered as a result of the above two major effects. However, the excess viscosity data of the three systems studied is not an agreement with the arguments based on the excess compressibility data probably due to cominance of the difference in sizes and shapes of the molecules on the viscous flow of the mixtures.

Basing on the experimental result, the schematic representation of the molecular interactions through the formation of hydrogen bonding is as follows.

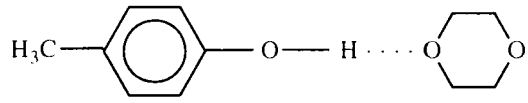
System 1 : P-cresol(1) + dimethyl sulfoxide(2)



System 2 : P-cresol(1) + dimethyl formamide(2)



System 3 : P-cresol(1) + 1, 4 dioxane(2)



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