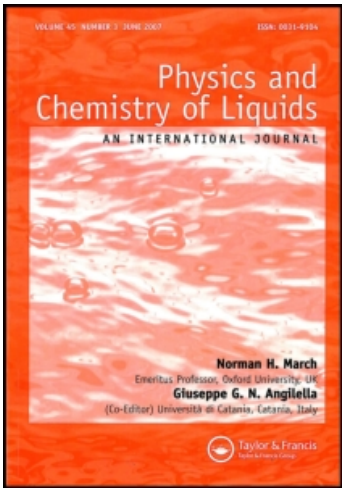

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A STUDY OF INTERACTIONS IN BINARY MIXTURES OF 1-HEPTANOL WITH SOME CHLORINATED ETHANES AND ETHENES FROM VISCOSITY MEASUREMENTS AT 303.15 K

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Viscosities for binary liquid mixtures of 1-heptanol with 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloroethene and tetrachloroethene were measured at 303.15 K. Excess viscosity (η^E) values are negative in all the systems over the whole composition range. Excess Gibbs free energy for activation of flow (G^E), strength of interaction parameter (d) and interaction energy (W_{visc}) were evaluated from experimental data.

KEY WORDS: Interaction energy, excess free energy.

INTRODUCTION

1-Heptanol, Chloroethanes (1,2-dichloroethane, 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane) and chloroethenes (trichloroethene and tetrachloroethene) are important as raw materials, solvents, cleaning agents etc. in industrial operations. In the present investigation the effect of successive chlorination, the presence of double bond on ethane molecule and interactions between unlike molecules are studied through viscosity data. Further, the study is extended to explain the interactions in terms of excess Gibbs free energy for activation of flow (G^E), strength of interaction parameter (d) and interaction energy (W_{visc}).

EXPERIMENTAL METHODS

Materials

1-Heptanol (Koch-Light) is further purified by fractional distillation. 1,2-dichloroethane (BDH), 1,1,1-trichloroethane (Koch-Light) and 1,1,2,2-tetrachloroethane (Riedel) were purified by the methods described by Ramanjaneyulu *et al.*[1] Trichloroethene

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Table 1 Physical constants of pure components at 303.15 K.

Components	*Density (g cm^{-3})*		*Viscosity (cP)*	
	Exp	*Lit*	*Exp*	*Lit*
1-Heptanol	0.81573	—	4.862	—
1,2-Dichloroethane	1.23828	1.23831	0.734	0.730
1,1,1-Trichloroethane	1.32094	1.32096	0.729	0.725
1,1,2,2-Tetrachloroethane	1.57857	1.57860	1.459	1.456
Trichloroethene	1.45134	1.45134	0.529	0.532
Tetrachloroethene	1.60636	1.60640	0.814	0.798

(BDH) and tetrachloroethene (BDH) were purified using the method described by Riddick and Bunger.[2] The measured densities and viscosities of the purified components are in good agreement with the literature data. The data are given in Table 1.

Viscosities

Viscosities of liquids and liquid mixtures were determined using Ostwald viscometers. The accuracy of the viscometer was checked by measuring the viscosities of pure benzene and cychohexene. The results show good agreement with those reported in the literature. Mixtures of various compositions were prepared by weight. A constant volume of mixture transferred into the viscometer and then inserted in a water thermostat controlled at 303.15 ± 0.01 K. The time of flow of the liquid through capillary was determined. Viscosity was then obtained from density (ρ) flow time (t) and constant of the viscometer (K_v) using the relation

$$\eta = K_v \rho_t. \tag{1}$$

Densities for pure components were determined experimentally. In case of mixtures densities were obtained from excess volumes reported elsewhere[3] using the equation,

$$\rho = \frac{xM_1 + (1 - x)M_2}{V^0 + V^E} \tag{2}$$

where x stands for mole fraction of 1-heptanol. M_1 and M_2 are molecular weights. V^0 and V^E denote the ideal molar volume and excess molar volume respectively.

THEORETICAL ASPECTS

Excess viscosity (η^E) of the mixtures were calculated from the relation of Fort and Moore,[4]

$$\eta^E = \eta_m - x\eta_1 - (1 - x)\eta_2 \tag{3}$$

where η_m is the viscosity of the mixture, η_1 and η_2 are the viscosities of 1-heptanol and the non-common component respectively.

Excess Gibbs free energy for activation of flow was calculated using Eyring's[5] relation,

$$G^E = RT[\ln \eta_m v_m - x \ln \eta_1 v_1 - (1 - x) \ln \eta_2 v_2] \quad (4)$$

The strength of interaction parameter (d) between the components of the mixture was calculated using the relation[6],

$$d = \frac{1}{x(1 - x)} [\ln \eta_m - x \ln \eta_1 - (1 - x) \ln \eta_2] \quad (5)$$

Katti and Chaudhari[7] deduced the following expression to show the variation of viscosity with molar volume and composition,

$$W_{visc} = \frac{RT}{x(1 - x)} [\ln \eta_m v_m - x \ln \eta_1 v_1 - (1 - x) \ln \eta_2 v_2] \quad (6)$$

where W_{visc} represents the interaction energy between the components.

RESULTS AND DISCUSSION

The values of density (ρ), viscosity (η_m), excess viscosity (η^E), excess Gibbs free energy for activation of flow (G^E), strength of interaction parameter (d) and interaction energy (W_{visc}) for all the systems are given in Table 2. Excess viscosity versus mole fraction of 1-heptanol plots are shown in Figures 1 and 2. The dependence of η^E on composition can be expressed by an empirical equation of the form,

$$\eta^E = x(1 - x)[a_0 + a_1(2x - 1) + a_2(2x - 1)^2] \quad (7)$$

where a_0, a_1 and a_2 are adjustable parameters. The values of the parameters, obtained by least square methods, are included in Table 3, along with the standard deviation, $\sigma(\eta^E)$.

The values of η^E are negative for all the systems over the entire composition range. The values of η^E may be explained on the basis of two effects; (i) depolymerization of self associated alcohol and (ii) formation of weak hydrogen bond of the form O—H···Cl. The actual values of the η^E depend upon the relative strength of the two opposing effects. The experimental results suggest that the former effect determines η^E in all the systems.

The algebraic values of η^E in mixtures containing chloroethanes and ethenes fall in the order, 1,2-dichloroethane < 1,1,1-trichloroethane < 1,1,2,2-tetrachloroethane and trichloroethene < tetrachloroethene.

This order suggests that increase of number of chlorine atoms in ethane or ethene molecule results in increase of η^E. The trend may be attributed to the increase of strength of interaction between unlike molecule as the number of chlorine atoms increases.

The values of d, G^E and W_{visc} run parallel with the η^E values except at lower and higher mole fractions. The variations of d, and W_{visc} with composition are considerable. Hence it may be concluded that Eqs. 5 and 6 are not capable of adequately representing the behaviour of the systems.

Table 2 Values of density (ρ), viscosity of the mixture (η_m), excess viscosity (η^E), excess Gibbs free energy for activation of flow (G^E), strength of the interaction parameter (d), and interaction energy (W_{visc}) at 303.15 K.

x	ρ ($g\ cm^{-3}$)	η_m (cP)	η^E (cP)	G^E ($Calmol^{-1}$)	d	W_{visc} ($Calmol^{-1}$)
			1-Heptanol + 1,2-dichloroethane			
0.1082	1.16219	0.852	−0.329	−25.36	−0.576	−262.80
0.1749	1.12132	0.918	−0.538	−50.90	−0.742	−352.74
0.3034	1.05261	1.082	−0.904	−91.39	−0.878	−432.51
0.4560	0.98433	1.415	−1.201	−100.66	−0.830	−405.72
0.5496	0.94812	1.752	−1.251	−79.22	−0.683	−320.08
0.6220	0.92257	2.078	−1.224	−60.42	−0.576	−257.00
0.7104	0.89390	2.581	−1.086	−33.55	−0.417	−163.10
0.7978	0.86797	3.174	−0.853	−12.77	−0.273	−79.17
0.8642	0.84969	3.699	−0.602	−0.18	−0.141	−1.53
0.9346	0.83153	4.286	−0.306	3.61	−0.039	59.08
			1-Heptanol + 1,1,1-trichloroethane			
0.1177	1.24086	0.974	−0.242	44.10	0.641	424.86
0.2075	1.18454	1.143	−0.444	40.06	0.341	243.67
0.3311	1.11306	1.392	−0.705	19.46	0.084	87.86
0.4385	1.05597	1.666	−0.875	5.60	−0.023	22.75
0.5262	1.01244	1.941	−0.963	−2.71	−0.077	−10.87
0.5911	0.98185	2.186	−0.986	−5.72	−0.097	−23.67
0.6407	0.94465	2.407	−0.970	−4.82	−0.092	−20.94
0.7497	0.91235	2.990	−0.838	−0.04	−0.060	−0.22
0.8365	0.87716	3.560	−0.626	3.67	−0.010	26.83
0.9206	0.84480	4.198	−0.336	4.70	0.053	64.30
			1-Heptanol + 1,1,2,2-tetrachloroethane			
0.1082	1.47171	1.677	−0.150	8.19	0.093	84.87
0.2331	1.35743	1.902	−0.350	−4.28	−0.087	−23.94
0.3041	1.29647	2.042	−0.452	−12.17	−0.141	−57.51
0.3446	1.26288	2.126	−0.506	−16.93	−0.170	−74.98
0.4479	1.18091	2.367	−0.616	−24.88	−0.224	−122.77
0.5205	1.12628	2.568	−0.662	−30.36	−0.245	−121.63
0.6548	1.03105	3.047	−0.640	−25.48	−0.229	−112.74
0.7810	0.90073	3.616	−0.501	−15.42	−0.189	−90.18
0.8562	0.85608	4.014	−0.359	−8.25	−0.150	−67.02
0.9304	0.81573	4.446	−0.179	−1.93	−0.086	−29.78
			1-Heptanol + trichloroethene			
0.1161	1.34223	0.734	−0.298	49.40	0.683	481.48
0.2045	1.26795	0.863	−0.552	32.65	0.221	200.68
0.2949	1.19873	0.989	−0.818	−3.43	−0.137	−16.50
0.3792	1.13949	1.166	−1.006	−15.54	−0.215	−66.02
0.4884	1.06951	1.459	−1.186	−26.02	−0.276	−104.21
0.5714	1.02072	1.767	−1.238	−22.29	−0.251	−91.02
0.6298	0.98842	2.030	−1.228	−17.65	−0.224	−75.69
0.7370	0.93312	2.643	−1.079	−4.64	−0.135	−23.96
0.8161	0.89527	3.197	−0.868	1.63	−0.075	10.86
0.9242	0.84717	4.119	−0.415	5.18	0.033	73.89
			1-Heptanol + tetrachloroethene			
0.1320	1.46901	1.080	−0.268	32.17	0.409	280.72
0.2375	1.36840	1.267	−0.508	16.93	0.099	93.48
0.3539	1.26571	1.511	−0.736	−0.90	−0.061	−3.94
0.4634	1.17624	1.807	−0.883	−10.66	−0.123	−42.86
0.5262	1.12772	2.016	−0.928	−12.41	−0.134	−49.78
0.5927	1.07841	2.259	−0.954	−15.78	−0.159	−65.39
0.6534	1.03513	2.548	−0.911	−9.22	−0.118	−40.71
0.7637	0.96046	3.149	−0.756	−1.93	−0.066	−10.69
0.8512	0.90458	3.725	−0.535	3.37	0.003	26.60
0.9246	0.85981	4.255	−0.302	2.83	0.026	40.60

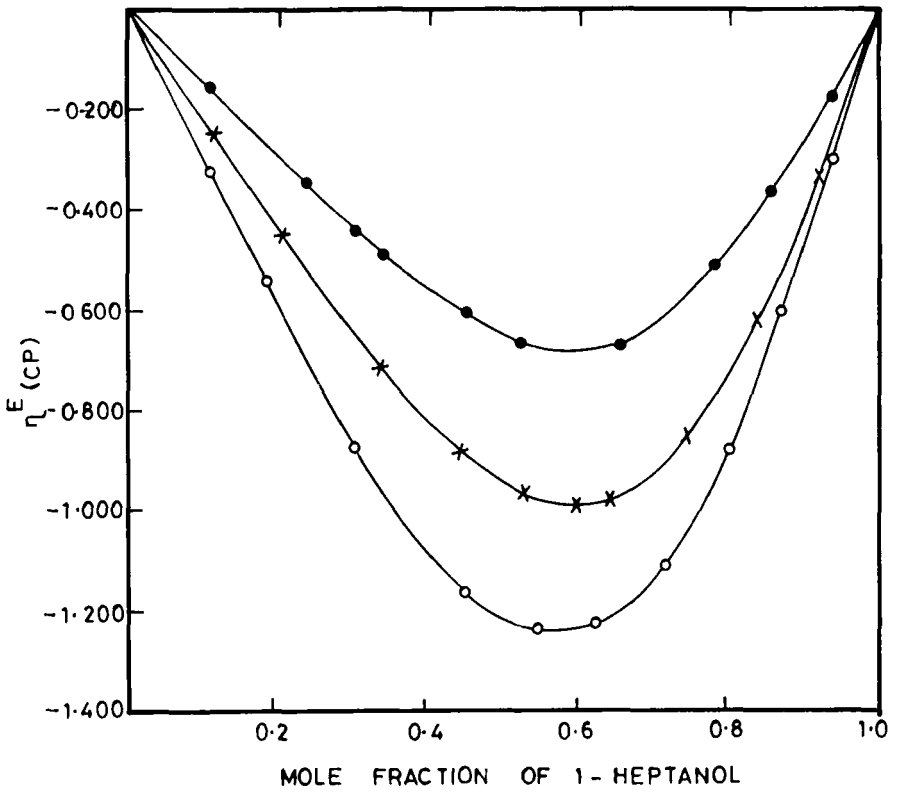

Figure 1 1-Heptanol + 1,2-dichloroethane (○), + 1,1,1-trichloroethane (×) and + 1,1,2,2-tetrachloroethane (●).

Table 3 Values of the parameters, a_0, a_1 and a_2 in Eq. (7) and the standard deviation, $\sigma(\eta^E)$ *at* 303.15 K.

System	a_0 (*cP*)	a_1 (*cP*)	a_2 (*cP*)	$\sigma(\eta^E)$ (*cP*)
1-Heptanol + 1,2-dichloroethane	−4.972	−1.125	1.189	0.009
1-Heptanol + 1,1,1-trichloroethane	−3.807	−1.518	0.594	0.009
1-Heptanol + 1,1,2,2-tetrachloroethane	−2.610	−0.857	0.687	0.006
1-Heptanol + trichloroethene	−4.805	−1.939	0.705	0.005
1-Heptanol + tetrachloroethene	−3.675	−1.321	0.676	0.006

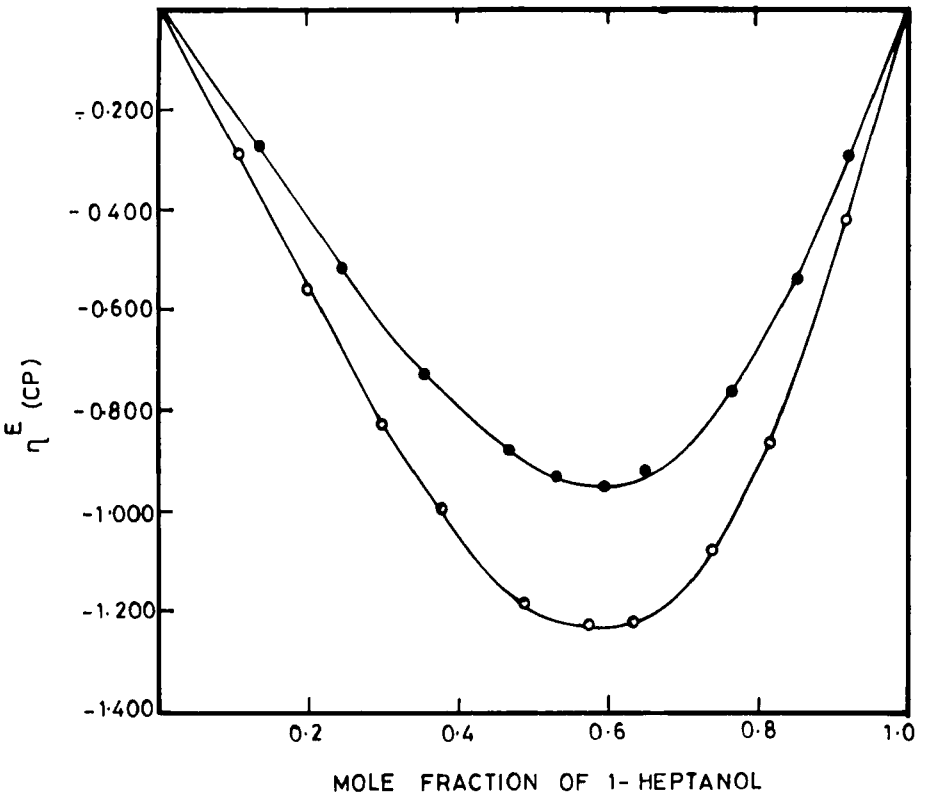

Figure 2 1-Heptanol + trichloroethene (○) and + tetrachloroethene (●).

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