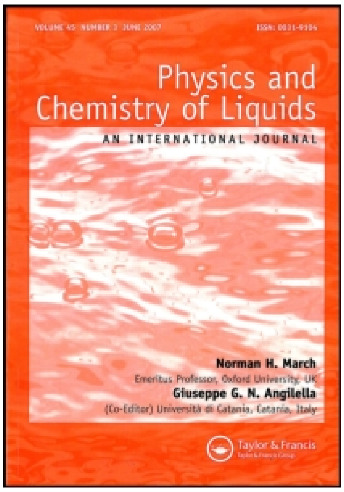

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Krishnan, K. Mohan , Ramachandran, D. , Venkateswarlu, P. and Raman, G. K.(1994) 'Viscosities of Binary Liquid Mixtures of Acetophenone with Aromatic Alcohols at 303.15 K', Physics and Chemistry of Liquids, 28: 3, 195 — 199

To link to this Article: DOI: 10.1080/00319109408034668

URL: http://dx.doi.org/10.1080/00319109408034668

Phys. Chem. Liq., 1994, Vol. 28, pp. 195–199
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VISCOSITIES OF BINARY LIQUID MIXTURES OF ACETOPHENONE WITH AROMATIC ALCOHOLS AT 303.15 K

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(Received 23 April 1994)

Viscosities of binary liquid mixtures of acetophenone with aromatic alcohols have been measured at 303.15 K. The values of excess viscosities are negative over the entire range of composition in all the systems studied. This can be attributed to the dissociation of self-associated alcohols by acetophenone. Further, the study has been extended to investigate intermolecular interactions in terms of excess free energy of mixing, strength of interaction parameter and interaction energy between the components.

KEY WORDS: Dissociation, intermolecular interactions.

1 INTRODUCTION

In recent years there has been considerable advancement in the experimental investigation of the excess thermodynamic properties of liquid mixtures. Excess thermodynamic functions have been used as a qualitative guide to predict the extent of complex formation in binary liquid mixtures of non-electrolytes. If the viscosity data for the mixtures could be obtained as a function of composition, the existence or non existence of specific interactions in them could be indicated by estimating the strength of interactions[1–3]. A number of workers[4–7] have utilised the direct approach developed by Grunberg and Nissan[2] and Katti and Chaudhri[3] to estimate the strength of interactions in binary mixtures of non-electrolytes from viscosity data. In continuation of our work[8] on solution properties we report in this paper the viscosity measurements for the study of molecular interactions of acetophenone with phenol, *o*-cresol, *m*-cresol, *p*-cresol and benzyl alcohol at 303.15 K. 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 ($W_{\text{visc.}}$).

2 EXPERIMENTAL

Acetophenone was purified by repeated crystallisation method described by Livingston and co-workers[9]. Phenol, *o*- and *p*-cresols were purified by the method described by Davison[10], *m*-cresol was dried over anhydrous sodium sulphate for long periods and fractionally distilled[11]. Benzyl alcohol was purified by fractional distillation at reduced pressure with the exclusion of air[12]. The purity of the samples was checked by measuring the densities and by comparing them with those reported in the literature[13-14].

Viscosity of liquids and liquid mixtures were determined at 303.15 K by an Ostwald Viscometer with an accuracy of ± 0.5%. The accuracy of the viscometer was checked by measuring the viscosities of benzene and cyclohexane. The results agree within ± 0.5% with those reported in the literature[13-14]. Mixtures of various compositions were prepared by mass. A constant volume of the mixture was transfered into the viscometer and then inserted in a water thermostat controlled at 303.15 (± 0.01 K). The viscosities were computed from flowtime (t), density (ρ) and the constant of the viscometer (k) using the equation.

$$\eta = K\rho t \tag{1}$$

The density of the pure components were measured with a pycnometer. In case of mixtures, densities were obtained from excess volumes[8] using the relation,

$$\rho = \frac{XM_1 + (1-X)M_2}{V^0 \pm V^E} \tag{2}$$

where X stands for molefraction of acetophenone, M_1 and M_2 are the molecular weights of components 1 and 2 respectively V^0 and V^E denote the ideal molar volume and excess molar volume respectively.

Excess viscosity of the mixtures were calculated from the relation of Fort and Moore[1]

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

where m is the viscosity of the mixture, 1 and 2 are the viscosities of acetophenone and the non common component respectively. X is molefraction of acetophenone. Grunberg and Nissan[2] formulated the following expression to define the interaction parameter, d,

$$d = \frac{1}{x(1-x)}[\ln \eta_m - x \ln \eta_1 - (1-x) \ln \eta_2] \tag{4}$$

Katti and Chaudhri[3] deduced the following expression to show the variation of viscosity with molar volumes and composition,

$$W_{\text{visc}} = \frac{RT}{x(1-x)}[\ln \eta V - x \ln \eta_1 V_1 - (1-x) \ln \eta_2 V_2] \tag{5}$$

where W_{visc} represents the interaction energy between the components. Excess Gibbs free energy for activation of flow (G^{*E}) was calculated using Eyring's relation[15].

$$G^{*E} = RT[\ln \eta V - x \ln \eta_1 V_1 - (1-x) \ln \eta_2 V_2] \tag{6}$$

3 RESULTS AND DISCUSSION

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

$$\eta^E = x(1 - x)\,[a_0 + a_1(2x - 1) + a_2(2x - 1)^2] \tag{7}$$

Table 1 Mole fraction (X), density (ρ), Viscosity of the mixture (η_m), excess viscosity (η^E), Strength of interaction parameter (d), Interaction energy (W_{visc}) and excess Gibbs free energy for activation of flow (G^{*E}) at 303.15 K.

X	ρ $g\ cm^{-3}$	η_m cP	η^E cp	G^{*E} $Cal\ mol^{-1}$	d	W_{visc} $Cal\ mol^{-1}$
			Acetophenone + phenol			
0.0000	1.06650	5.516	—	—	—	—
0.0901	1.06188	4.976	−0.179	10.5303	0.1680	128.57
0.2182	1.05559	4.319	−0.323	27.5466	0.2239	161.47
0.3102	1.05123	3.905	−0.368	39.7283	0.2650	185.73
0.4048	1.04679	3.519	−0.375	51.4875	0.3123	213.73
0.5083	1.04196	3.131	−0.348	62.0322	0.3704	248.23
0.5936	1.03798	2.839	−0.298	69.3420	0.4363	287.49
0.7241	1.03189	2.404	−0.211	69.9112	0.5409	349.91
0.7583	1.03033	2.295	−0.182	68.2383	0.5782	372.28
0.8846	1.02452	1.887	−0.084	46.9412	0.7244	459.76
1.0000	1.01940	1.509	—	—	—	—
			Acetophenone + *o*-cresol			
0.0000	1.03769	6.043	—	—	—	—
0.1100	1.03738	5.369	−0.175	21.1599	0.3510	216.14
0.2168	1.03626	4.793	−0.267	45.4180	0.4067	267.48
0.3155	1.03467	4.305	−0.308	60.4028	0.4566	279.64
0.4164	1.03281	3.832	−0.323	74.7399	0.5030	307.57
0.4556	1.03204	3.653	−0.324	78.7040	0.5192	317.35
0.5575	1.02996	3.206	−0.309	85.2279	0.5660	345.47
0.6919	1.02713	2.635	−0.271	79.2383	0.6096	371.66
0.7608	1.02559	2.358	−0.236	69.7752	0.6291	383.38
0.9488	1.02091	1.668	−0.073	17.7644	0.5996	365.52
1.0000	1.01940	1.509	—	—	—	—
			Acetophenoneone + *m*-cresol			
0.0000	1.02604	9.802	—	—	—	—
0.1390	1.02639	8.438	−0.211	66.8738	0.9233	560.08
0.1802	1.02637	8.063	−0.245	86.0301	0.9606	582.47
0.2700	1.02615	7.268	−0.295	124.9032	1.0457	633.70
0.4388	1.02540	5.843	−0.320	183.8734	1.2331	746.50
0.4644	1.02528	5.630	−0.321	190.3706	1.2645	765.46
0.5506	1.02475	4.927	−0.313	205.7226	1.3803	831.54
0.7407	1.02320	3.390	−0.269	195.9901	1.6873	1020.25
0.8321	1.02213	2.684	−0.217	158.1483	1.8733	1132.06
0.9266	1.02079	2.000	−0.118	87.2023	2.1229	1282.39
1.0000	1.01940	1.509	—	—	—	—

Table 1 (*continued*)

X	ρ g cm^{-3}	η_m cP	η^E cp	G^{*E} Cal mol^{-1}	d	W_{visc} Cal mol^{-1}
			Acetophenone + *p*-cresol			
0.0000	1.02517	12.076	—	—	—	—
0.1137	1.02614	10.702	−0.173	70.0432	1.1476	694.87
0.1526	1.02634	10.248	−0.215	92.7759	1.1851	717.52
0.3364	1.02639	8.205	−0.316	189.4561	1.4030	848.82
0.4260	1.02602	7.246	−0.328	226.9098	1.5346	928.06
0.4932	1.02556	6.538	−0.326	249.1805	1.6493	997.12
0.5636	1.02494	5.804	−0.316	265.6239	1.7873	1080.21
0.7580	1.02272	3.823	−0.243	257.4381	2.3243	1403.70
0.8099	1.02206	3.310	−0.208	235.5542	2.5350	1530.57
0.9433	1.02020	2.026	−0.082	106.6257	3.3027	1993.00
1.0000	1.01940	1.509	—	—	—	—
			Acetophenone + Benzyl alcohol			
0.0000	1.03762	4.645	—	—	—	—
0.0742	1.03617	4.331	−0.081	8.4178	0.1955	122.53
0.2566	1.03275	3.618	−0.222	24.1579	0.2025	126.61
0.3107	1.03176	3.420	−0.251	27.0054	0.2016	126.08
0.4505	1.02920	2.937	−0.295	30.1147	0.1943	121.63
0.5280	1.02778	2.685	−0.304	28.5640	0.1828	114.62
0.5727	1.02692	2.544	−0.305	26.3205	0.1711	107.56
0.7494	1.02369	2.036	−0.259	11.5470	0.0947	61.49
0.8383	1.02211	1.820	−0.196	3.9631	0.0412	29.23
0.9234	1.02067	1.638	−0.111	−2.1571	−0.0579	−30.51
1.0000	1.01940	1.509	—	—	—	—

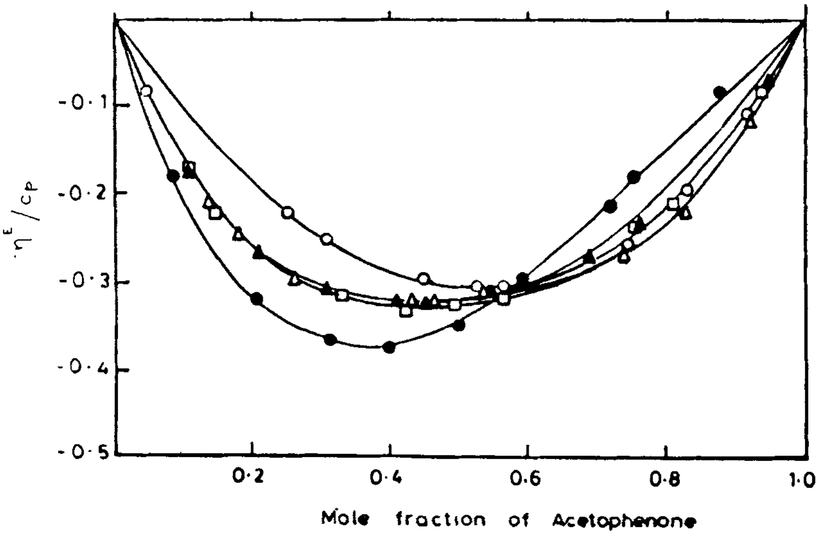

Figure 1 Viscosities of Acetophenone + Phenol (●), + *o*-Cresol (▲), + *m*-Cresol (△), + *p*-Cresol (□), + Benzyl Alcohol (○).

Table 2 Values of parameters, a_0, a_1 and a_2 of the Eq. (7) and the standard deviation, $\sigma(\eta^E)$ at 303.15 K.

System	c_0	c_1	c_2	$\sigma(\eta^E)$
	C_p			
Acetophenone + phenol	-1.418	0.874	-0.035	0.006
Acetophenone + *p*-cresol	-1.300	0.254	-0.482	0.005
Acetophenone + *m*-cresol	-1.276	0.181	-0.776	0.006
Acetophenone + *o*-cresol	-1.274	0.301	-0.539	0.006
Acetophenone + Benzyl alcohol	-1.215	-0.162	-0.222	0.005

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 2, along with the Standard deviation $\sigma(\eta^E)$.

The values of η^E are negative over the entire range of molefraction. The values of η^E may be explained on the basis of two effects:

(i) Depolymerisation of self associated alcohols and
(ii) formation of weak hydrogenbond between the —OH and carbonyl group. The actual value of η^E depend upon the strength of two opposing effects. The experimental results suggest that the former effect determines in all the systems.

The variations of d, and W_{visc} with composition are considerable. The free flow of these mixtures suggests the flexibility of the alcohol molecules in the liquid mixture structure. Hence, it can be concluded the Equations 4 and 5 are not capable of adequate representing the behaviour of the systems. The G^{*E} values included in Table 1 suggest that the behaviour of the systems is in tune with the observations made by Reed and Taylor[16].

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