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A COMPARISON OF DIFFERENT THEORIES OF VISCOUS FLOW FOR BINARY LIQUID MIXTURES OF TOLUENE WITH CHLOROBENZENE, BENZYLALCOHOL AND N-HEXANOL AT DIFFERENT TEMPERATURES

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ABSTRACT

The viscosity in binery liquid mixtures of toluene with chlorobenzene, benzyl alcohol and n-hexanol has been evaluated at 30, 40, 50 and 60°C by Naidu, ubbelohde, Grunberg-Nissam and Katti-Chaudhuri's method and the result has been compared with the experimental values. The result has been discussed in terms of inter-molecular interaction. The agreement is better for toluene with non-associated liquids.

An attempt has been made to compare the relative merits of Naidu, Ubbelohde, Grunberg-Nissam and Katti-Chaudhuri's method for the theoretical evaluation of viscosity in binary liquid mixtures of toluene with chlorobenzene, benzyl alcohol and *n*-hexanol at 30°, 40°, 50° and 60°C, over the complete composition range, with the experimental value. Furthermore, the deviation of the theoretical value from the experimental results has been discussed in terms of intermolecular-interaction. The required experimental data for the comparison have been taken from the literature[1]. Naidu[2] obtained the following relation for the theoretical value of viscosity for binary liquid mixture

$$\ln \eta_m = x_1^2 \ln \eta_1 + x_2^2 \ln \eta_2 + 2x_1 x_2 \ln \eta_{12}. \quad (1)$$

where η_1 and η_2 are the viscosities of the pure liquid components whose mole fractions are x_1 and x_2. η_m is the viscosity of the mixture and η_{12} is the viscosity at equimolar concentration. The value of η_{12} is obtained by the relation $\eta_{12} = 0.5\eta_1 + 0.5\eta_2$. Hind *et al*[3] and Frankel[6] used the following expressions for the viscosity of a liquid mixture, respectively,

$$\eta_m = x_1^2 \eta_1 + 2x_1 x_2 \eta_{12} + x_2^2 \eta_2, \quad (2)$$

$$\log \eta_m = x_1 \log \eta_1 + x_2 \log \eta_2 + 2x_1 x_2 \log \eta_{12}. \quad (3)$$

The viscosity of a liquid mixture according to Grunberg and Nissam[4] and Katti-Chaudhuri[5] is obtained by following two different equations, respectively;

$$\ln \eta_m = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d \quad (4)$$

and

$$\ln \eta m(a) \cdot V_m = x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2 + x_1 x_2 \frac{W_{vis}}{RT} \quad (5)$$

where $$W_{vis} = \frac{RT}{x_1 x_2} \ln \left[\frac{V_m}{V_1^{x_1} V_2^{x_2}} + x_1 x_2 d \right]. \quad (6)$$

In (4), d is the approximate measure of strength of interaction and in equations (5) and (6), V_1, V_2 and V_m represent the molar volumes of the component 1, 2 and mixture, respectively. W_{vis} stands for interaction energy between the components at temperature T.

The experimental and theoretical values of viscosities obtained by different methods, for the title binaries, at different temperatures are listed in tables 1, 2 and 3, respectively. Table 1 indicates that at all the mole fractions and at all the temperatures studied, Naidu and Ubbelohde relations give values more comparable with the experimental values than Grunberg and Nissam and Katti-Chaudhuri's relations. For the systems toluene + benzyl alcohol and tolune + *n*-hexanol, only Frenkel[6], Ubbelohde and

Table 1. *Experimental and theoretical values of viscosity for binary mixture of toluene + chlorobenzene at different temperatures.*

T/°C	x_1^*	η_{mix} (C.P.) Expt.	η_m (C.P.) (eq. 1)	η_m (C.P.) (eq. 2)	η_m (C.P.) (eq. 4)	η_m (C.P.) (eq. 5)
	0.000	0.7184	—	—	—	—
	0.0961	0.6999	0.6999	0.7009	0.6975	0.6974
	0.1930	0.6793	0.6813	0.6834	0.6749	0.6748
	0.2907	0.6641	0.6630	0.6657	0.6586	0.6584
30	0.3894	0.6454	0.6447	0.6478	0.6391	0.6395
	0.4889	0.6300	0.6232	0.6298	0.6234	0.6233
	0.5893	0.6109	0.6084	0.6116	0.6046	0.6044
	0.6906	0.5935	0.5904	0.5932	0.5880	0.5879
	0.7928	0.5753	0.5725	0.5747	0.5711	0.5710
	0.8959	0.5561	0.5548	0.5560	0.5537	0.5536
	1.0000	0.5372	—	—	—	—
	0.0000	0.6469	—	—	—	—
	0.0961	0.6302	0.6304	0.6313	0.6281	0.6280
	0.1930	0.6128	0.6139	0.6156	0.6091	0.6089
	0.2907	0.5947	0.5975	0.5998	0.5898	0.5897
	0.3894	0.5789	0.5811	0.5838	0.5733	0.5735
40	0.4889	0.5763	0.5649	0.5677	0.5704	0.5703
	0.5893	0.5475	0.5487	0.5515	0.5420	0.5419
	0.6906	0.5414	0.5326	0.5351	0.5364	0.5364
	0.7928	0.5159	0.5166	0.5186	0.5120	0.5121
	0.8959	0.5005	0.5008	0.5019	0.4984	0.4893
	1.0000	0.4851	—	—	—	—
	0.0000	0.5724	—	—	—	—
	0.0961	0.5575	0.5575	0.5584	0.5571	0.5558
	0.1930	0.5432	0.5427	0.5443	0.5398	0.5397
50	0.2907	0.5310	0.5280	0.5301	0.5266	0.5256
	0.3894	0.5111	0.5133	0.5158	0.5061	0.5106
	0.4889	0.5008	0.4987	0.5014	0.4955	0.4953
	0.5893	0.4829	0.4842	0.4866	0.4780	0.4779
	0.6906	0.4715	0.4698	0.4721	0.4670	0.4675
	0.7928	0.4539	0.4555	0.4572	0.4506	0.4538
	0.8959	0.4396	0.4412	0.4423	0.4377	0.4403
	1.0000	0.4272	—	—	—	—
	0.0000	0.5198	—	—	—	—
	0.0961	0.5058	0.5066	0.5073	0.5042	0.5041
	0.1930	0.4927	0.4929	0.4948	0.4897	0.4897
	0.2907	0.4816	0.4803	0.4821	0.4778	0.4778
	0.3894	0.4654	0.4672	0.4694	0.4610	0.4610
60	0.4889	0.4545	0.4542	0.4565	0.4499	0.4499
	0.5893	0.4394	0.4413	0.4435	0.4350	0.4349
	0.6906	0.4259	0.4284	0.4304	0.4218	0.4197
	0.7928	0.4117	0.4157	0.4172	0.4088	0.4088
	0.8959	0.4000	0.4030	0.4039	0.3984	0.3984
	1.0000	0.3908	—	—	—	—

Table 2. *Toluene + benzyl alcohol*

T/°C	x_1^*	η_{exp} (C.P.)	η_m (C.P.) (eq. (3))	η_m (C.P.) (eq. (2))	η_m (C.P.) (eq. (1))
	0.0000	4.605	—	—	—
	0.0973	3.563	4.4102	4.2092	4.0730
	0.1952	2.788	4.0731	3.8109	3.5329
	0.2937	2.226	3.6251	3.4102	3.0041
	0.3927	1.758	3.1075	3.0075	2.5037
	0.4924	1.386	2.5629	2.6020	2.0439
30	0.5927	1.107	2.0333	2.1940	1.6339
	0.6936	0.8989	1.5501	1.7835	1.2786
	0.7951	0.7359	1.1349	1.3706	0.9792
	0.8972	0.6154	0.7975	0.9553	0.7335
	1.0000	0.5372	—	—	—
	0.0000	3.533	—	—	—
	0.0973	2.793	3.2916	3.2364	3.1397
	0.1952	2.237	2.9851	2.9380	2.7430
	0.2937	1.781	2.6335	2.6378	2.3552
40	0.3927	1.440	2.2593	2.336	1.9870
	0.4924	1.150	1.8835	2.0321	1.6462
	0.5927	0.9561	1.5251	1.7264	1.3391
	0.6936	0.7776	1.199	1.4189	1.0692
	0.7951	0.6508	0.9146	1.1095	0.8377
	0.8972	0.5511	0.6767	0.7984	0.6438
	1.0000	0.4851	—	—	—
	0.0000	2.646	—	—	—
	0.0973	2.117	2.3890	2.4301	2.3721
	0.1952	1.730	2.1209	2.2128	2.0808
	0.2937	1.403	1.8506	1.9943	1.8043
	0.3927	1.157	1.5067	1.7946	1.5411
50	0.4924	0.9401	1.3361	1.5534	1.2598
	0.5927	0.7918	1.1047	1.3309	1.0725
	0.6936	0.6576	0.8965	1.1070	0.8734
	0.7951	0.5456	0.7140	0.8818	0.6940
	0.8972	0.4771	0.5578	0.6552	0.5514
	1.0000	0.4272	—	—	—
	0.0000	2.037	—	—	—
	0.0973	1.683	1.7942	1.8767	1.8309
	0.1952	1.406	1.5679	1.7155	1.6254
	0.2937	1.180	1.3587	1.5534	1.4249
60	0.3927	0.9701	1.1623	1.3903	1.2333
	0.4924	0.8112	0.9949	1.2262	1.0535
	0.5927	0.6838	0.8402	1.0610	0.8879
	0.6936	0.5757	0.7033	0.8949	0.7384
	0.7951	0.4829	0.5835	0.7278	0.6056
	0.8972	0.4265	0.4796	0.5596	0.4726
	1.0000	0.3905	—	—	—

Naidu's relations have been used for the theoretical evaluation. Since density data were not available for these systems, Katti-Chaudhuri's equation, which needs molar volume for theoretical calculation, could not be used. Table 2 and 3 show that values obtained by Naidu's relation are nearer to the experimental values as compared to the other two methods. As regards the numerical values of viscosities for the binary formed by toluene as component (1) and anyone of the remaining liquids as component (2) the

Table 3. *Toluene + n-hexanol*

T/°C	x_1°	$\eta_{exp.}$ (C.P.)	η_m(C.P.) (eq. (3))	η_m(C.P.) (eq. (2))	η_m(C.P.) (eq. (1))
	0.0000	3.765	—	—	—
	0.1151	2.859	3.5166	3.3934	3.2735
	0.2265	2.167	3.1676	3.0339	2.8001
	0.3342	1.692	2.7615	2.6862	2.3610
	0.4384	1.351	2.2454	2.3499	1.9639
30	0.5394	1.099	1.9271	2.0239	1.6177
	0.6372	0.8820	1.5514	1.7082	1.3183
	0.7321	0.7364	1.2222	1.4019	1.0645
	0.8241	0.6235	0.9448	1.1049	0.8530
	0.9133	0.5592	0.7180	0.8170	0.6791
	1.0000	0.5372	—	—	—
	0.0000	2.934	—	—	—
	0.1151	2.206	2.6599	2.6521	2.5803
	0.2265	1.701	2.3548	2.3793	2.2138
	0.3342	1.341	2.0409	2.1155	1.8869
	0.4384	1.097	1.7354	1.8603	1.5911
40	0.5394	0.9164	1.4505	1.6130	1.2185
	0.6372	0.7593	1.1941	1.3735	1.1006
	0.7321	0.6439	0.9695	1.1411	0.9047
	0.8241	0.5569	0.7777	0.9158	0.7389
	0.9133	0.5069	0.6173	0.6974	0.6002
	1.0000	0.4851	—	—	—
	0.0000	2.169	—	—	—
	0.1151	1.661	1.8970	1.9685	1.9119
	0.2265	1.321	1.8447	1.7744	1.6669
	0.3342	1.057	1.4152	1.5868	1.4395
	0.4384	0.8845	1.2097	1.4053	1.2325
50	0.5394	0.7532	1.0274	1.2294	1.0475
	0.6372	0.6516	0.8690	1.0591	0.8844
	0.7321	0.5418	0.7313	0.8938	0.7423
	0.8241	0.4674	0.6132	0.7335	0.6200
	0.9133	0.4336	0.5126	0.5782	0.5156
	1.0000	0.4272	—	—	—
	0.0000	1.655	—	—	—
	0.1151	1.333	1.4002	1.5094	1.4719
	0.2265	1.069	1.2025	1.3685	1.2982
	0.3342	0.8832	1.0315	1.2323	1.1368
60	0.4384	0.7193	0.8884	1.1005	0.9892
	0.5394	0.6029	0.7679	0.9729	0.8559
	0.6372	0.5141	0.6663	0.8492	0.7370
	0.7321	0.4508	0.5800	0.7292	0.6318
	0.8241	0.4046	0.5067	0.6129	0.5398
	0.9133	0.3954	0.4442	0.5001	0.4597
	1.0000	0.3905	—	—	—

values of η_m change smoothly from η_1 to η_2 as X_1 varies from 0 to 1 for each binary system studied. The difference between the experimental and theoretical values of viscosity obtained by different methods are small for toluene and non-associated liquids while these are larger for the associated liquids *n*-hexanol and benzyl alcohol.

A smaller deviation of the theoretical value of viscosity from the experimental result for non-associated liquids indicates that during the flow process, the structuredness or order as a result of the formation of activated complex, is slightly more than that in the initial state. On the other hand, the larger deviation for associated liquids shows that the formation of activated complex during the viscous flow requires the destruction of a more orderly initial hydrogen-bonded structure causing a decrease in the overall order.

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