Prediction of viscosity of multicomponent liquid mixtures

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Viscosities of three quaternary, viz. n-hexadecane + n-tetradecane + n-hexane + 2-bromobutane (I), n-hexadecane + carbon tetrachloride + benzene + n-hexane (II) and n-hexadecane + n-tetradecane + 4-methylcyclohexanone + n-hexane (III) and eleven ternary liquid mixtures (IA-D, IIA-D and IIIA-C) have been evaluated theoretically, using various empirical relations (Frenkel, Kendall-Munroe, Bingham and Additive relations) applicable to binary mixtures. The theoretical values of viscosity of these mixtures are compared with the experimental viscosities given in literature. The results of calculation show that the viscous behaviour of these liquid mixtures having constituent components with likelihood of better interactions with each other, can be best explained by Frenkel relation as it takes into account all the possible major interactions. Still better results by Frenkel relation are obtained when some small molecules like CCl$_4$ is one of the components of the mixture (II) which can take up interstitial positions resulting in enhanced interaction. The presence of planar molecules, like benzene with its π-electron cloud above and below the ring, certainly inhibits the interaction between the components to some extent and results in somewhat ideal behaviour of mixtures. This is evident for some systems where Kendall-Munroe and Additive relations give better results than those given by Frenkel relation. The presence of substituent and polar groups on one of the components affects the extent of interaction more than when they are present in a cyclic molecule than on a straight chain hydrocarbon. Thus, the presence of bromine in system (I) and the ternary mixtures still allows interaction to a greater extent since in the possible compact structure 2-bromobutane can fit with bromine protruding out. However, the presence of polar and substituent groups in cyclic molecule (4-methylcyclohexanone) does not allow interaction and also inhibits the interaction of other components resulting in ideal mixing and thus better results are obtained in system (III) and the corresponding ternaries (IIIA-C) by Kendall-Munroe and Additive relations.

Knowledge of viscosity of multicomponent liquid mixtures is of particular interest to chemical industry and chemical engineering. Computation of viscosity of binary liquid mixtures[1-3] has been an active field of interest and not much work has been done on the application of various models to ternary quaternary liquid mixtures. An attempt has now been made to extend various viscosity models, viz. Frenkel[4], Kendall-Munroe[5], Additive[6,7], Bingham[8] and Hind-Ubbelhode to ternary and quaternary liquid mixtures, viz. n-hexadecane + n-tetradecane + n-hexane + 2-bromobutane (I), n-hexadecane + carbon tetrachloride + benzene + n-hexane (II) and n-hexadecane + n-tetradecane + n-hexane + 4-methylcyclohexanone (III) and their eleven ternary liquid mixtures containing permutations of these liquids. The data have been analysed in the light of structure of molecules and the interactions involved.

Theoretical

Bingham[8] proposed Eq. (1) for binary liquid mixtures which gives the ideal viscosity of the mixture,

$$\eta = x_1\eta_1 + x_2\eta_2 \qquad \ldots (1)$$

For n-component mixture. Eq. (1) can be rewritten as,

$$\eta = \sum_{i=1}^{n} x_i\eta_i \qquad \ldots (2)$$

where x_i, η_i are respectively the mol fraction and viscosity of the pure components.

Following Kendall and Munroe[5], Eq. (3) gives the viscosity for multicomponent system,

$$\ln \eta = \sum_{i=1}^{n} x_i \ln \eta_i \qquad \ldots (3)$$

Additive relation based on Arrhenius model[6]

and Eyring's model[7] for the viscosity of pure liquid can be modified to multicomponent system as,

$$\ln \eta_v = \sum_{i=1}^{n} x_i \ln \eta_i V_i \qquad \ldots (4)$$

where V_i is the volume of ith component.

These relations were proposed considering the ideal mixing of solutions, which is not always true. Taking into consideration the interaction between the molecules, Frenkel[4], with the help of Eyring's model, developed the logarithmic relation (5) for non-ideal binary liquid mixtures:

$$\ln \eta = x_1^2 \ln \eta_1 + x_2^2 \ln \eta_2 + 2 x_1 x_2 \ln \eta_{12} \qquad \ldots (5)$$

where η_{12} is a constant.

This equation when extended to ternary and quaternary liquid mixtures takes the following forms (6A) and (6B) respectively,

$$\ln \eta = x_1^2 \ln \eta_1 + x_2^2 \ln \eta_2 + x_3^2 \ln \eta_3 + 2(x_1 x_2 \ln \eta_{12}$$
$$+ x_2 x_3 \ln \eta_{23} + x_3 x_1 \ln \eta_{31}) + 3(x_1 x_2 x_3 \ln \eta_{123}) \ldots (6A)$$

$$\ln \eta = x_1^2 \ln \eta_1 + x_2^2 \ln \eta_2 + x_3^2 \ln \eta_3 + x_4^2 \ln \eta_4 +$$
$$2(x_1 x_2 \ln \eta_{12} + x_1 x_3 \ln \eta_{13} + x_1 x_4 \ln \eta_{14} + x_2 x_3 \ln \eta_{23}$$
$$+ x_2 x_4 \ln \eta_{24} + x_3 x_4 \ln \eta_{34}) + 3(x_1 x_2 x_3 \ln \eta_{123}$$
$$+ x_1 x_2 x_4 \ln \eta_{124} + x_2 x_3 x_4 \ln \eta_{234} + x_1 x_3 x_4 \ln \eta_{134})$$
$$+ 4(x_1 x_2 x_3 x_4 \ln \eta_{1234}) \qquad \ldots (6B)$$

For ternary and quaternary liquid mixtures, the relationship suggested by Hind et al.[9] takes the forms (7A) and (7B), respectively,

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + x_3^2 \eta_3 + 2(x_1 x_2 \eta_{12} + x_1 x_3 \eta_{13}$$
$$+ x_2 x_3 \eta_{23}) + 3 x_1 x_2 x_3 \eta_{123}) \qquad \ldots (7A)$$

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + x_3^2 \eta_3 + x_4^2 \eta_4 + 2(x_1 x_2 \eta_{12} + x_1 x_3 \eta_{13}$$
$$+ x_1 x_4 \eta_{14} + x_2 x_3 \eta_{23} + x_3 x_4 \eta_{34} + x_2 x_4 \eta_{24})$$
$$+ 3(x_1 x_2 x_3 \eta_{123} + x_1 x_3 x_4 \eta_{134} + x_2 x_3 x_4 \eta_{234}$$
$$+ x_1 x_2 x_4 \eta_{124}) + 4 x_1 x_2 x_3 x_4 \eta_{1234} \qquad \ldots (7B)$$

Results and Discussion

Viscosities of three quaternary liquid mixtures (I-III) and their eleven ternary mixtures have been computed using Frenkel relation (Eqs 6A and

6B), Kendall-Munroe relation (Eq. 3), Bingham relation (Eq. 2), Additive relation (Eq. 4) and Hind-Ubbelhode relation (Eqs 7A and 7B). The values of viscosity, molecular weight and molar volume of the pure components are taken from the literature[10]. The experimental data were taken from the work of Heric and Brewer[11,12]. Incorporation of 2-bromobutane and 4-methylcyclohexanone is of particular interest as it facilitates the study of viscous behaviour of mixtures in the presence of polar groups and the effect of substituent groups in the hydrocarbon chain. Moreover, the presence of more polar groups like bromine and keto group is not likely to add to the compactness of the system and therefore, it is anticipated that such a system must show ideal behaviour. The viscosities computed by all the empirical equations are recorded in Tables 1 and 2 along with the average percentage deviation (D) and standard percentage error (S) for all the three quaternary and eleven ternary liquid mixtures.

Quaternary liquid mixture: n-hexadecane + n-tetradecane + n-hexane + 2-bromobutane (I) and its ternary liquid mixtures

For this quaternary system, the standard percentage error for Frenkel's relation, Kendall-Munroe's relation, Bingham relation, Additive relation and Hind's relation are 3.907, 14.176, 21.407, 19.832 and 39.114 respectively. Taking into consideration the inevitable experimental error and limitations of various theories the results obtained from all the relations except those of Hind's relation, are comparable.

It is interesting to note that the ternary liquid mixtures, i.e. n-hexane + n-tetradecane + n-hexadecane (IA), n-hexane + n-tetradecane + 2-bromobutane (IB), n-hexadecane + n-tetradecane + 2-bromobutane (IC) and n-hexadecane + n-hexane + 2-bromobutane (ID) also follow almost the same trend. Frenkel relation gives the best results while the Hind's relation gives rather poor results for wider use.

The best results obtained by Frenkel's relation are due to the fact that it incorporates all the possible major interactions. Excellenet results by Frenkel's relation implies that even 2-bromobutane interacts significantly. Thus, it seems that 2-bromobutane molecule also fits with other components with bromine protruding out of the compact structure.

As expected the results based on Kendal-Munroe's Additive and Bingham's relations are good but not very encouraging. These relations were

Table 1 – Experimental and theoretically computed values of viscosity using Bingham, Additive, Kendall-Munroe, Frenkel and Hind relations for various multicomponent systems at 298.15°K

X_1	X_2	X_3	ρ	η_{expt}	Theoretical viscosity				
					Bingham relation η_B	Additive relation η_{Add}	Kendall-Munroe relation η_{KM}	Hind relation η_H	Frenkel relation η_F
				n-Hexadecane + n-Tetradecane + n-Hexane + 2-Bromobutane (I)					
0.7546	0.0501	0.0887	0.7869	2.3119	2.5013	1.9329	2.0382	2.5702	2.3847
0.5219	0.0935	0.1770	0.8066	1.6842	1.9622	1.2610	1.3744	2.1631	1.7778
0.3130	0.3337	0.1431	0.8067	1.5989	1.8145	1.2498	1.3503	2.2249	1.7398
0.0674	0.5638	0.1590	0.8042	1.3752	1.5455	1.1096	1.4113	1.6599	1.3969
0.3966	0.1125	0.2090	0.8264	1.3875	1.6694	1.0137	1.1164	1.7770	1.4199
0.0823	0.4292	0.2144	0.8220	0.1738	1.3642	0.9115	0.9889	1.5440	1.2146
0.2166	0.2392	0.2632	0.8239	1.1419	1.3978	0.8581	0.9382	1.6931	1.0788
0.2801	0.1217	0.2727	0.8390	1.1050	1.3753	0.8089	0.8904	1.5770	1.0875
0.1089	0.2958	0.2545	0.8444	1.0141	1.1217	0.7764	0.8466	1.5270	0.9830
0.1448	0.1703	0.2339	0.8883	0.9265	1.1214	0.7066	0.8242	1.3448	0.9051
0.2282	0.0673	0.5401	0.7738	0.7986	1.0915	0.7048	0.6396	1.2563	0.7719
0.1432	0.1724	0.3743	0.8310	0.8551	1.0832	0.6515	0.7069	1.3185	0.8610
0.1412	0.1652	0.3190	0.8567	0.8653	1.0820	0.6642	0.7231	1.3134	0.8610
0.1588	0.1099	0.2448	0.9047	0.8653	1.0617	0.7471	0.7269	1.2586	0.8695
0.0988	0.1966	0.3858	0.8338	0.7964	1.0060	0.6212	0.6718	1.2154	0.8067
0.1011	0.1799	0.2312	0.9053	0.8559	1.0276	0.6692	0.7288	1.2178	0.8701
0.0534	0.2467	0.5551	0.7633	0.7065	0.9235	0.5592	0.5958	1.0557	0.7264
0.0486	0.2253	0.1076	0.9652	0.8794	0.8655	0.7028	0.7661	1.1685	0.8394
0.1388	0.1070	0.3460	0.8710	0.7773	0.9803	0.6055	0.6559	1.2381	0.7970
0.1685	0.0491	0.1208	0.9878	0.8704	1.0265	0.8507	0.7389	1.0207	0.8548
0.0898	0.1626	0.3229	0.8784	0.7711	0.9485	0.6099	0.6589	1.1355	0.8269
0.0877	0.1090	0.5261	0.8124	0.6227	0.8075	0.5051	0.5372	0.7764	0.6956
0.0813	0.1038	0.1917	0.9749	0.7448	0.8729	0.6080	0.6543	0.9918	0.7433
0.0554	0.0674	0.1443	1.0422	0.6774	0.7654	0.5812	0.6156	0.8303	0.7264
0.0625	0.0654	0.6820	0.7680	0.4889	0.6366	0.4213	0.4399	0.7161	0.5297
0.0354	0.0457	0.0992	1.1026	0.6332	0.6945	0.5709	0.5767	0.7239	0.6291
0.0401	0.0456	0.7924	0.7308	0.4133	0.5211	0.3732	0.3844	0.5594	0.4424
0.0226	0.0283	0.8855	0.6974	0.3610	0.4262	0.2840	0.3438	0.4395	0.3787
				n-Hexadecane + Carbontetrachloride + Benzene + n-Hexane (II)					
0.5779	0.1432	0.1108	0.8153	1.7521	2.0152	1.2211	1.4496	2.1713	1.8804
0.4270	0.1728	0.1939	0.8348	1.3515	1.6413	1.1676	1.1173	1.8659	1.4126
0.2048	0.2877	0.2946	0.9233	0.8959	1.1272	0.7202	0.8117	1.2843	0.9501
0.1718	0.5529	0.1503	1.0886	1.0083	1.1517	0.8155	0.9106	1.3076	1.0246
0.1567	0.1345	0.5734	0.8742	0.7896	0.9875	0.6650	0.7464	1.1298	0.8390
0.1941	0.1855	0.1562	0.8305	0.7175	0.9932	0.5845	0.6402	1.1827	0.7714
0.1296	0.3986	0.2776	1.0114	0.7919	0.9810	0.6929	0.7611	1.1691	0.8843
0.1153	0.3568	0.3490	0.9995	0.7618	0.9382	0.6763	0.7393	1.1162	0.8116

Contd

Table 1 – Experimental and theoretically computed values of viscosity using Bingham, Additive, Kendall-Munroe, Frenkel and Hind relations for various multicomponent systems at 298.15°K – *Contd.*

X_1	X_2	X_3	ρ	η_{expt}	Theoretical viscosity				
					Bingham relation η_B	Additive relation η_{Add}	Kendall-Munroe η_{KM}	Hind relation η_H	Frenkel relation η_F
0.1318	0.2700	0.2672	0.9100	0.6806	0.9061	0.6026	0.6582	1.1117	0.7975
0.1030	0.2856	0.3697	0.9486	0.6788	0.8675	0.7350	0.6736	1.0154	0.7409
0.1045	0.2304	0.4075	0.9133	0.6525	0.8499	0.5926	0.6531	1.9204	1.7158
0.1059	0.3654	0.2579	0.9841	0.6906	0.8893	0.6318	0.6843	1.0050	1.7539
0.0499	0.1559	0.6857	0.9281	0.6281	0.7396	0.6112	0.6453	0.8059	0.6724
0.0376	0.0967	0.7809	0.9008	0.6068	0.6991	0.6011	0.6283	0.7467	0.6490
0.0648	0.2098	0.5662	0.9411	0.6316	0.7765	0.6108	0.6514	0.8778	0.6869
0.0662	0.5369	0.2370	1.1377	0.7368	0.8762	0.7005	0.7429	0.9922	0.7870
0.0154	0.0674	0.8460	0.8937	0.5771	0.6401	0.5911	0.6048	0.6559	0.6148
0.0709	0.3385	0.3326	0.9880	0.6231	0.7992	0.6058	0.6455	0.9485	0.6874
0.0653	0.2243	0.4281	0.9165	0.5704	0.7442	0.5645	0.6006	0.8281	0.6371
0.0449	0.6744	0.1523	1.2508	0.7595	0.8748	0.7432	0.7761	0.8090	0.8635
0.0289	0.4056	0.4717	1.1090	0.6721	0.7665	0.6728	0.6962	0.8605	0.7116
0.0673	0.4077	0.2382	1.0215	0.6189	0.8020	0.6092	0.6463	0.9424	0.7267
0.0687	0.2565	0.2394	0.8967	0.5269	0.7149	0.5185	0.5485	0.9504	0.5931
0.0280	0.7538	0.1170	1.3300	0.7730	0.8651	0.7722	0.7946	0.9041	0.8207
0.0530	0.2047	0.2157	0.8511	0.4645	0.6328	0.5831	0.4908	0.7397	0.5251
0.0307	0.1033	0.6043	0.8314	0.4531	0.5988	0.6045	0.5113	0.7072	0.5312
0.0397	0.4704	0.1559	1.0594	0.5684	0.7382	0.5886	0.6126	0.8173	0.6481
0.0399	0.1499	0.1367	0.7921	0.4045	0.5392	0.4507	0.4234	0.6022	0.4520

n-Hexadecane + n-Tetradecane + 4-Methylcyclohexanone + n-Hexane (III)

X_1	X_2	X_3	ρ	η_{expt}	η_B	η_{Add}	η_{KM}	η_H	η_F
0.7415	0.0539	0.1186	0.7726	2.3951	2.5998	2.1656	2.2741	2.6709	2.5737
0.5415	0.0931	0.1659	0.7690	1.8510	2.1791	1.5526	1.6670	2.4036	2.1246
0.0456	0.7441	0.1149	0.7643	1.7602	1.9041	1.6450	1.7097	1.9858	1.8859
0.3004	0.3576	0.1705	0.7676	1.7171	1.9911	1.5051	1.6028	2.0956	2.0508
0.2920	0.3351	0.1832	0.7678	1.6615	1.9448	1.4388	1.5369	1.1993	1.7121
0.4280	0.1206	0.2264	0.7714	1.6508	1.9941	1.3820	1.4951	2.2879	2.0934
0.0667	0.5834	0.1754	0.7654	1.5339	1.2498	1.3773	1.4570	2.1025	1.8550
0.2374	0.0740	0.5490	0.8106	1.5458	1.8692	1.3924	1.5118	1.9247	1.8069
0.1036	0.4529	0.2396	0.7698	1.4418	1.7084	1.5464	1.3705	1.9775	1.6987
0.3071	0.1319	0.2951	0.7744	1.4094	1.7706	1.1865	1.2980	2.0654	1.7215
0.1996	0.2418	0.2856	0.7716	1.3187	1.6572	1.1391	1.2282	1.9029	1.6271
0.1831	0.1331	0.4298	0.7890	1.2695	1.6078	1.1327	1.2213	1.8698	1.5629
0.1159	0.3232	0.2710	0.7679	1.2294	1.5528	1.0775	1.1561	1.8481	1.4980
0.1632	0.1892	0.3755	0.7811	1.2357	1.5810	1.1008	1.1857	1.8875	1.5378
0.1040	0.1069	0.5983	0.8160	1.2624	1.5640	1.2063	1.2834	1.7373	1.5325
0.1699	0.2017	0.2661	0.7638	1.1113	1.4776	0.9541	1.0252	1.7893	1.3600
0.1661	0.1307	0.3903	0.7807	1.1351	1.5048	1.0177	1.0932	1.9475	1.4224

Contd

Table 1 – Experimental and theoretically computed values of viscosity using Bingham, Additive, Kendall-Munroe, Frenkel and Hind relations for various multicomponent systems at 298.15°K – *Contd.*

X_1	X_2	X_3	ρ	η_{expt}	Theoretical viscosity				
					Bingham relation η_B	Additive relation η_{Add}	Kendall-Munroe η_{KM}	Hind relation η_H	Frenkel relation η_F
0.1445	0.1694	0.3417	0.7726	1.0909	1.4493	0.9616	1.0312	1.7363	1.3561
0.0995	0.1664	0.3606	0.7722	0.9791	1.3447	1.0622	0.9533	1.5906	1.2318
0.1066	0.1953	0.2463	0.7536	0.9179	1.2650	1.0001	1.8444	1.5160	1.1541
0.1019	0.1097	0.3952	0.7752	0.9318	1.2953	0.8590	0.9098	1.5083	1.1099
0.0887	0.0955	0.4156	0.7773	0.8931	1.2603	0.8429	0.8883	1.4494	1.1271
0.0650	0.2698	0.1323	0.7338	0.8108	0.1051	0.6725	0.7134	1.1957	0.9143
0.0989	0.1034	0.2249	0.7402	0.7113	1.0373	0.6472	0.6607	1.2059	0.8453
0.0446	0.1034	0.2249	0.7402	0.7113	1.0373	0.6472	0.6607	1.2059	0.8453
0.0446	0.0498	0.4563	0.7791	0.7447	1.1104	0.7618	0.7854	1.2121	0.8678
0.0741	0.0779	0.1608	0.7208	0.5740	0.8524	0.5163	0.5384	0.9598	0.6601
0.0434	0.0455	0.1158	0.7010	0.4503	0.6502	0.4244	0.4358	0.6881	0.5028

n-Hexadecane + n-Tetradecane + n-Hexane (I-A or III-D)

X_1	X_2	X_3	ρ	η_{expt}	η_B	η_{Add}	η_{KM}	η_H	η_F
0.0650	0.0796		0.6857	0.4631	0.6182	0.3876	0.4026	0.6423	0.4574
0.1028	0.1119		0.6976	0.5654	0.7805	0.4454	0.4683	0.8297	0.5614
0.1046	0.1763		0.7064	0.6538	0.9006	0.5041	0.5333	0.9728	0.6612
0.1521	0.1151		0.7060	0.6582	0.9226	0.4986	0.5288	0.9924	0.6590
0.1650	0.1831		0.7158	0.7862	0.0798	0.5840	0.6223	1.1870	0.8051
0.0878	0.3651		0.7246	0.9111	1.1917	0.6980	0.7412	1.2871	0.9545
0.2118	0.2258		0.7259	0.9491	1.2856	0.7059	0.7546	1.4320	1.0088
0.3274	0.0947		0.7271	0.9851	1.3710	0.7119	0.7654	1.4685	1.0262
0.1297	0.4208		0.7340	1.1144	1.4071	0.8593	0.9112	1.5406	1.1926
0.2648	0.2924		0.7372	1.2078	1.5513	0.9129	0.9725	1.7378	1.3189
0.3995	0.1514		0.7389	1.2787	1.6718	0.9445	1.0117	1.8196	1.3805
0.1105	0.5396		0.7411	1.3054	1.5664	1.0440	1.0986	1.6800	1.3968
0.2522	0.3998		0.7436	1.4001	1.7084	1.1022	1.1644	1.8994	1.5431
0.3777	0.2696		0.7453	1.4750	1.8228	1.1417	1.2109	2.0182	1.6313
0.5182	0.1243		0.7472	1.5625	1.9516	1.1892	1.2663	2.0769	1.6933

n-Tetradecane + n-Hexane + 2-Bromobutane (I-B)

X_1	X_2	X_3	ρ	η_{expt}	η_B	η_{Add}	η_{KM}	η_H	η_F
0.5081	0.2082		0.8250	1.1103	1.2802	0.8859	0.9576	1.3685	1.1125
0.4355	0.2524		0.8337	0.9918	1.1580	0.7822	0.8464	1.2589	0.9852
0.3167	0.2528		0.8803	0.8342	0.9772	0.6699	0.7244	1.0786	0.8251
0.3418	0.3469		0.8211	0.8203	0.9903	0.6547	0.7046	1.0989	0.8187
0.2586	0.3389		0.8691	0.7194	0.8658	0.5930	0.6352	0.9697	0.7207
0.1460	0.1960		1.0003	0.6468	0.7327	0.5686	0.6009	0.7882	0.6472
0.1522	0.3748		0.9043	0.5815	0.6944	0.5130	0.5400	0.7738	0.5925
0.1563	0.5875		0.7998	0.5170	0.6439	0.4529	0.4736	0.7132	0.5267
0.0953	0.1450		1.0659	0.6098	0.6692	0.5575	0.5810	0.7001	0.6115

Contd

Table 1 — Experimental and theoretically computed values of viscosity using Bingham, Additive, Kendall-Munroe, Frenkel and Hind relations for various multicomponent systems at 298.15°K — *Contd.*

X_1	X_2	X_3	ρ	η_{expt}	Theoretical viscosity				
					Bingham relation η_B	Additive relation η_{Add}	Kendall-Munroe η_{KM}	Hind relation η_H	Frenkel relation η_F
0.0889	0.3222		0.9700	0.5305	0.6122	0.4957	0.5142	0.6619	0.5477
0.0935	0.5088		0.8670	0.4762	0.5694	0.4433	0.4588	0.6251	0.4940
0.1018	0.7088		0.7639	0.4331	0.5287	0.3957	0.4079	0.5689	0.4421

n-Hexadecane + n-Tetradecane + 2-Bromobutane (I-C)

X_1	X_2	X_3	ρ	η_{expt}	η_B	η_{Add}	η_{KM}	η_H	η_F
0.0635	0.0791		1.1068	0.7806	0.8420	0.6501	0.6953	0.8666	0.7463
0.0889	0.0966		1.0724	0.8548	0.9321	0.6850	0.7427	0.9720	0.8143
0.1071	0.1579		1.0184	0.9783	1.0708	0.7537	0.8299	1.1418	0.9375
0.1439	0.1067		1.0258	0.9813	1.0849	0.7488	0.8260	1.1506	0.9354
0.1631	0.1740		0.9760	1.1264	1.2352	0.8373	0.9319	1.3426	1.0863
0.0976	0.3315		0.9325	1.2068	1.3111	0.9242	1.0250	1.4165	1.1892
0.2114	0.2210		0.9294	1.2919	1.4274	0.9628	1.0755	1.5788	1.2883
0.3055	0.1082		0.9360	1.3319	1.4910	0.9675	1.0882	1.6016	1.3022
0.1232	0.4021		0.8923	1.3778	1.4824	1.0624	1.1740	1.6167	1.3796
0.2344	0.2714		0.8993	1.4263	1.5615	1.0733	1.1944	1.7410	1.4465
0.3556	0.1414		0.9014	1.5061	1.6667	1.1037	1.2371	1.8111	1.5028
0.1197	0.5444		0.8449	1.5958	1.6901	1.2957	1.4059	1.8151	1.6235
0.2265	0.3893		0.8602	1.6124	1.7211	1.2527	1.3752	1.9145	1.6541
0.3794	0.2805		0.8466	1.7984	1.9377	1.4113	1.5452	2.1444	1.8783
0.5152	0.1200		0.8538	1.8669	2.0330	1.4268	1.5763	2.1618	1.8958

n-Hexadecane + n-Hexane + 2-Bromobutane (I-D)

X_1	X_2	X_3	ρ	η_{expt}	η_B	η_{Add}	η_{KM}	η_H	η_F
0.4873	0.2392		0.8233	1.38758	1.7169	0.9962	1.1019	1.8419	1.4155
0.3755	0.2712		0.8492	1.11891	1.4290	0.8059	0.8933	1.5701	1.1353
0.2961	0.2359		0.8873	0.97905	1.2399	0.7158	0.7988	1.3682	0.9816
0.3115	0.3461		0.8438	0.95320	1.2491	0.6939	0.7639	1.3938	0.9641
0.2462	0.3508		0.8683	0.83096	1.0846	0.6238	0.6818	1.2211	0.8364
0.1712	0.1628		0.9553	0.76071	0.9474	0.5995	0.6776	1.0212	0.7725
0.1839	0.3727		0.8876	0.70688	0.9231	0.5607	0.6050	1.0423	0.7182
0.1875	0.5936		0.7873	0.62790	0.8731	0.4940	0.5282	0.9687	0.6358
0.1262	0.1921		1.0110	0.69300	0.8271	0.5769	0.6162	0.8919	0.6875
0.1334	0.3807		0.9098	0.62070	0.7948	0.5191	0.5526	0.8915	0.6343
0.1342	0.6035		0.8030	0.54476	0.7373	0.4541	0.4795	0.8206	0.5558
0.0796	0.1302		1.0827	0.64117	0.7272	0.5650	0.5925	0.7593	0.6351
0.0794	0.3194		0.9752	0.55557	0.6762	0.5016	0.5245	0.7360	0.5747
0.0922	0.5131		0.8652	0.51254	0.6565	0.4524	0.4733	0.7297	0.5298
0.0849	0.7122		0.7701	0.44774	0.5851	0.3963	0.4113	0.6332	0.4565

Contd

Table 1 — Experimental and theoretically computed values of viscosity using Bingham, Additive, Kendall-Munroe, Frenkel and Hind relations for various multicomponent systems at 298.15°K — *Contd.*

X_1	X_2	X_3	ρ	η_{expt}	Theoretical viscosity				
					Bingham relation η_B	Additive relation η_{Add}	Kendall-Munroe η_{KM}	Hind relation η_H	Frenkel relation η_F
				n-Hexadecane + Carbontetrachloride + Benzene (II-A)					
0.4489	0.2860	0.	0.9031	1.6725	1.7922	1.1896	1.4032	1.9476	1.6504
0.2523	0.2780	0.	0.9481	1.6999	1.3067	0.8717	1.0167	1.4571	1.1720
0.2648	0.4474	0.	1.0234	1.3029	1.3875	0.9548	1.1100	1.5432	1.2710
0.1551	0.4100	0.	1.0574	1.0180	1.1069	0.8145	0.9152	1.2331	1.0162
0.1484	0.6257	0.	1.1786	1.1107	1.1543	0.8857	0.9867	1.2501	1.0741
0.0625	0.1453	0.	0.9484	0.7364	0.8009	0.6659	0.7086	0.8337	0.7422
0.0670	0.3242	0.	1.0618	0.8052	0.8649	0.7190	0.7666	0.9253	0.8112
0.0704	0.5477	0.	1.1994	0.8956	0.9395	0.7908	0.8427	1.0067	0.8917
0.0723	0.7648	0.	1.3290	0.9894	1.0084	0.8666	0.9218	1.0496	0.9622
0.3318	0.2817	0.	0.9273	1.3573	1.5031	0.9813	1.1584	1.6681	1.3585
0.2072	0.3805	0.	1.0158	1.1275	1.2262	0.8576	0.9843	1.3746	1.1165
0.1063	0.2240	0.	0.9768	0.8410	0.9318	0.7152	0.7851	1.0046	1.8479
0.1056	0.4362	0.	1.1035	0.9240	0.9929	0.7806	0.8535	1.0893	0.9242
0.1062	0.6374	0.	1.2198	1.0079	1.0540	0.8496	0.9257	1.1333	0.9913
				Carbontetrachloride + n-Hexane + Benzene (II-B)					
0.7166	0.1195	0.	1.3320	0.6869	0.7796	0.7329	0.7384	0.8049	0.7465
0.5342	0.1531	0.	1.1958	0.6089	0.7153	0.6634	0.6704	0.7613	0.6687
0.5718	0.2210	0.	1.1916	0.5753	0.7055	0.6402	0.6483	0.7526	0.6532
0.3570	0.1237	0.	1.0876	0.5850	0.6718	0.6313	0.6378	0.7131	0.6335
0.3833	0.2487	0.	1.0882	0.5305	0.6411	0.5972	0.5896	0.7043	0.5845
0.4172	0.4249	0.	1.0214	0.4523	0.5969	0.5189	0.5271	0.6473	0.5379
0.1919	0.2414	0.	0.9328	0.4767	0.5867	0.5400	0.5491	0.6339	0.5462
0.1976	0.4138	0.	0.8870	0.4141	0.5354	0.4775	0.4868	0.5926	0.4861
0.2544	0.5706	0.	0.8816	0.3879	0.5038	0.4380	0.4452	0.5495	0.4533
0.6331	0.1482	0.	1.2628	0.6438	0.7461	0.6928	0.6998	0.7830	0.7038
0.4643	0.1965	0.	1.1319	0.5636	0.6812	0.6244	0.6321	0.7369	0.6283
0.3215	0.4557	0.	0.9530	0.4267	0.5590	0.4879	0.4963	0.6178	0.5006
0.3071	0.2359	0.	1.0128	0.5063	0.6225	0.5687	0.5772	0.6821	0.5712
0.2415	0.1371	0.	1.0025	0.5472	0.6335	0.5966	0.6033	0.6705	0.6002
				n-Hexadecane + Benzene + n-Hexane (II-C)					
0.5315	0.2836	0.	0.7681	1.4969	1.9375	1.1096	1.4049	2.0562	1.7323
0.2957	0.3586	0.	0.7575	1.1189	1.3307	0.6568	0.8803	1.4868	1.1063
0.2691	0.4941	0.	0.7738	0.9790	1.3390	0.6648	0.9618	1.4731	1.1594
0.1850	0.2552	0.	0.7293	0.9532	0.9620	0.4824	0.6059	1.0746	0.7430
0.1873	0.4706	0.	0.7621	0.8310	1.0985	0.5419	0.7740	1.2269	0.9294
0.1557	0.7030	0.	0.8000	0.7607	1.1516	0.5766	0.9310	1.2174	1.0384

Contd

Table 1 − Experimental and theoretically computed values of viscosity using Bingham, Additive, Kendall-Munroe, Frenkel and Hind relations for various multicomponent systems at 298.15°K − *Contd.*

X_1	X_2	X_3	ρ	η_{expt}	Theoretical viscosity				
					Bingham relation η_B	Additive relation η_{Add}	Kendall-Munroe η_{KM}	Hind relation η_H	Frenkel relation η_F
0.0798	0.2586	0.	0.7122	0.7069	0.6731	0.3824	0.4757	0.7312	0.5427
0.0757	0.4724	0.	0.7478	0.6279	0.7909	0.4204	0.5976	0.8598	0.6814
0.0707	0.6666	0.	0.7859	0.6930	0.8945	0.4641	0.7331	0.9472	0.8120
0.0686	0.8205	0.	0.8212	0.6207	0.9817	0.5091	0.8656	1.0082	0.9209
0.3605	0.3979	0.	0.7685	0.5448	1.5337	0.7825	1.0699	1.6812	1.3256
0.2238	0.4657	0.	0.7653	0.6412	1.1965	0.5883	0.8384	1.3343	1.0161
0.1281	0.3120	0.	0.7292	0.5556	0.8389	0.4363	0.5651	0.9343	0.6701
0.1221	0.5406	0.	0.7665	0.5125	0.9605	0.4849	0.7185	1.0553	0.8324
0.1074	0.7202	0.	0.8007	0.4477	1.0284	0.5216	0.8478	1.0852	0.9359

n-Hexadecane + Carbontetrachloride + n-Hexane (II-D)

0.4597	0.2910	0.	0.8682	1.4881	1.7434	1.0636	1.1978	1.8855	1.5131
0.2868	0.4576	0.	0.9681	1.1455	1.3659	0.8536	0.9626	1.5087	1.1748
0.1999	0.2122	0.	0.8218	0.7003	0.9772	0.5536	0.5981	1.0834	0.7387
0.1798	0.4855	0.	1.0007	0.8589	1.0868	0.7037	0.7733	1.2122	0.9237
0.0897	0.1824	0.	0.7953	0.4755	0.6544	0.4282	0.4472	0.7051	0.5101
0.0844	0.4337	0.	0.9772	0.5882	0.7916	0.5532	0.5842	0.8667	0.6714
0.0790	0.6400	0.	1.1474	0.7237	0.9014	0.6837	0.7256	0.9619	0.8106
0.0764	0.8002	0.	1.2950	0.8933	0.9910	0.8108	0.8619	1.0231	0.9237
0.3904	0.3706	0.	0.9106	1.3775	1.5999	0.9821	1.1131	1.7471	1.3861
0.2345	0.4277	0.	0.9552	0.9518	1.2032	0.7418	0.8240	1.3474	1.0099
0.1344	0.2691	0.	0.8562	0.5964	0.8304	0.5129	0.5467	0.9223	0.6504
0.1201	0.5150	0.	1.0334	0.7257	0.9395	0.6456	0.6951	1.0356	0.8081
0.1137	0.7014	0.	1.1863	0.8875	1.0344	0.7784	0.8425	1.0972	0.9364

n-Hexadecane + 4-Methylcyclohexanone + n-Hexane (III-A)

0.5434	0.2260	0.	0.7730	1.7397	2.0972	1.4240	1.5462	2.2380	1.9483
0.4168	0.2992	0.	0.7752	1.4509	1.8436	1.1937	1.3024	2.0197	1.6816
0.3271	0.2734	0.	0.7640	1.1298	1.5614	0.9322	1.0109	1.7391	1.3404
0.3206	0.4019	0.	0.7861	1.3273	1.7129	1.1388	1.2388	1.8908	1.5745
0.2610	0.3656	0.	0.7752	1.0877	1.5002	0.9396	1.0130	1.6774	1.3170
0.1914	0.4028	0.	0.7770	0.9531	1.3568	0.8615	0.9171	1.5124	1.1764
0.1890	0.6346	0.	0.8232	1.3539	1.6559	1.2634	1.3513	1.7611	1.5768
0.1338	0.2296	0.	0.7347	0.6274	0.9690	0.5708	0.5975	1.0663	0.7475
0.1379	0.6508	0.	0.8253	1.2239	1.5359	1.1688	1.2326	1.6302	1.4462
0.0919	0.1563	0.	0.7123	0.5009	0.7565	0.4631	0.4784	0.8102	0.5684
0.0864	0.3793	0.	0.7616	0.6730	1.0354	0.6674	0.6895	1.1224	0.8535
0.0854	0.5480	0.	0.8001	0.8684	1.2551	0.8853	0.9159	1.3404	1.1144
0.0917	0.7706	0.	0.8513	1.3081	1.5662	1.3034	1.3559	1.6145	1.5057

Contd

Table 1 – Experimental and theoretically computed values of viscosity using Bingham, Additive, Kendall-Munroe, Frenkel and Hind relations for various multicomponent systems at 298.15°K – *Contd.*

X_1	X_2	X_3	ρ	η_{expt}	Theoretical viscosity				
					Bingham relation η_B	Additive relation η_{Add}	Kendall-Munroe η_{KM}	Hind relation η_H	Frenkel relation η_F
n-Tetradecane + 4-Methylcyclohexanone + n-Hexane (III-B)									
0.5390	0.2386	0.	0.7671	1.3252	1.5744	1.1939	1.2706	1.6887	1.4919
0.4512	0.2676	0.	0.7663	1.1779	1.4557	1.0548	1.1245	1.5914	1.3533
0.3679	0.2532	0.	0.7582	0.9854	1.2878	0.8778	0.9327	1.4288	1.1504
0.3590	0.3680	0.	0.7780	1.1306	1.4233	1.0454	1.1138	1.5674	1.3328
0.2829	0.3659	0.	0.7728	0.9721	1.2845	0.9038	0.9567	1.4297	1.1668
0.2355	0.1579	0.	0.7279	0.6568	0.9254	0.5845	0.6128	1.0155	0.7490
0.2185	0.3936	0.	0.7739	0.8754	1.2059	0.8420	0.8843	1.3392	1.0792
0.2247	0.5961	0.	0.8153	1.2101	1.4841	1.1952	1.2620	1.5800	1.4305
0.1596	0.2203	0.	0.7323	0.5979	0.8720	0.5664	0.5875	0.9591	0.7103
0.1640	0.4218	0.	0.7758	0.8124	0.1456	0.8012	0.8340	1.2601	1.0138
0.1594	0.6152	0.	0.8175	1.0879	1.3925	1.1001	1.1476	1.4808	1.3202
0.1176	0.1552	0.	0.7124	0.4732	0.7111	0.4711	0.4847	0.7641	0.5664
0.1151	0.3404	0.	0.7535	0.6345	0.9509	0.6412	0.6604	1.0361	0.7993
0.1162	0.5470	0.	0.8005	0.8786	1.2253	0.9103	0.9395	1.3109	1.1149
n-Hexadecane + n-Tetradecane + 4-Methylcyclohexanone (III-C)									
0.5022	0.1640	0.	0.7916	2.3165	2.4186	2.1559	2.3220	2.6045	2.5351
0.3808	0.1507	0.	0.8056	2.1390	2.2367	1.9626	2.1412	2.4185	2.3353
0.4167	0.2428	0.	0.7915	0.2296	2.3318	2.0847	2.2430	2.5648	2.4871
0.3187	0.2235	0.	0.8036	2.0974	2.1810	1.9274	2.0964	2.4015	2.3133
0.2188	0.0956	0.	0.8348	1.9096	1.9766	1.7476	1.9037	2.0739	2.0052
0.2503	0.2438	0.	0.8088	2.0060	2.0916	1.8526	2.0170	2.3003	2.2120
0.3010	0.4590	0.	0.7815	2.1604	2.2658	2.0862	2.2010	2.4900	2.4203
0.1506	0.1188	0.	0.8427	1.8291	1.8887	1.6965	1.8331	1.9771	1.9175
0.1832	0.2761	0.	0.8130	1.9252	2.0096	1.7924	1.9483	2.1945	2.1125
0.2044	0.4558	0.	0.7900	2.0296	2.1245	1.9343	2.0674	2.3386	2.2623
0.0953	0.0897	0.	0.8600	1.7424	1.7950	1.6510	1.7563	1.8421	1.8031
0.1180	0.2057	0.	0.8333	1.8355	1.8823	1.6972	1.8355	1.9932	1.9319
0.1177	0.3866	0.	0.8067	1.8781	1.9666	1.7775	1.9217	2.1191	2.0521

developed considering the ideal mixing of solutions which in reality is not feasible.

Hind's relation though considers the possible interactions, fails to give good results. This discrepancy is due to the fact that this relation takes into account the simple additivity of viscosities of all the components, hence results in very high values of viscosity.

Quaternary liquid mixture: n-hexadecane + carbon tetrachloride + benzene + n-hexane (II) and its ternary liquid mixtures (IIA-IID)

The ternary liquid mixtures employed are n-hexadecane + carbon tetrachloride + benzene (IIA), carbon tetrachloride + n-hexane + benzene (IIB), n-hexadecane + benzene + n-hexane (IIC)

Table 2 − Comparison of various viscosity relations

No.	System	D% Average percentage deviation S% Standard percentage error				
		Frenkel's relation	Kendall & Munroe's relation	Additive relation	Bingham relation	Hind-Ubbelhode's relation
I	n-hexadecane + n-tetradecane + n-hexane + 2-bromobutane	3.121 3.907	13.582 14.176	19.017 19.832	19.925 21.407	35.521 39.114
IA or IIID	n-hexadecane + n-tetradecane + n-hexane	5.412 6.437	18.586 18.716	23.220 23.384	31.206 31.881	42.386 42.935
IB	n-tetradecane + n-hexane + 2-bromobutane	1.291 1.772	8.950 9.847	13.855 14.822	17.862 18.282	28.616 29.287
IC	n-hexadecane + n-tetradecane + 2-bromobutane	2.508 2.999	15.186 15.304	23.061 23.221	8.981 9.114	17.646 17.920
ID	n-hexadecane + n-hexane- + 2-bromobutane	1.644 1.861	13.416 14.293	19.540 20.536	27.360 28.036	39.952 40.966
II	n-hexadecane + carbontetrachloride + benzene + n-hexane	9.286 10.082	5.732 8.307	9.504 13.147	24.321 25.541	41.831 45.113
IIA	n-hexadecane + carbontetrachloride + benzene	1.119 1.511	9.744 10.489	18.871 19.922	7.377 7.866	16.727 17.452
IIB	Carbontetrachloride + n-hexane + benzene	12.777 13.259	12.566 12.945	11.264 11.590	22.142 22.964	31.642 32.838
IIC	n-hexadecane + benzene + n-hexane	18.565 22.836	16.304 21.442	32.654 34.008	30.791 35.406	40.794 45.055
IID	n-hexadecane + carbontetrachloride + n-hexane	6.657 7.768	9.284 11.294	16.290 18.099	25.985 27.605	37.423 39.301
III	n-hexadecane + n-hexane + n-tetradecane + 4-methylcyclohexanone	18.485 19.601	5.243 5.858	9.750 10.503	28.428 30.564	45.750 48.918
IIIA	n-hexadecane + 4-methylcyclohexanone + n-hexane	19.007 19.577	5.220 6.434	9.353 11.219	32.167 37.904	47.438 47.716
IIIB	n-tetradecane + 4-methylcyclohexanone + n-hexane	19.314 19.808	3.691 4.165	5.632 6.735	34.342 35.585	46.457 47.716
IIIC	n-hexadecane + n-tetradecane + 4-methylcyclohexanone	8.641 9.045	0.889 1.217	6.377 6.601	4.086 4.143	12.135 12.505

and n-hexadecane + carbon tetrachloride + n-hexane (IID).

A close examination of standard percentage error values (Table 2) reveals that Frenkel's relation gives better results for those ternary systems which contain carbon tetrachloride as a constituent. System IIC which does not contain carbon tetrachloride shows a higher deviation of 22.84%. This behaviour can be understood in the light of small size of carbon tetrachloride which permits greater interactions.

It should be noted that interactions are to some extent inhibited by the presence of benzene molecule to its planar structure and presence of π-electron cloud. This ultimately, may lead to an ideal behaviour. But this drift towards ideality is counteracted by the presence of carbon tetrachloride and consequently we get the intermediate value.

Again Hind-Ubbelhode's relation fails to give any encouraging results while those of Kendall-Munroe's, Additive and Bingham's relation are comparatively better with values coming within the experimental error.

Quaternary liquid mixture: *n*-hexadecane + *n*-tetradecane + *n*-hexane   4-methylcyclohexanone (*III*) and its ternary liquid mixtures (*IIIA-IIID*)

This system has 4-methylcyclohexanone as one of its components. The presence of this component in the mixture is of particular interest as it seems to affect the results of Frenkel's relation.

Systems III, IIIA, IIIB and IIIC containing 4-methyl-cyclohexanone as a constituent fail to yield very encouraging results (Table 1) by Frenkel's relation, which till now for all systems gave the best agreement. This discrepancy appears to be due to the presence of 4-methylcyclohexanone as a common constituent. The good agreement was due to the incorporation of two-body and three-body interactions. But owing to ring structure, polarity and steric hindrance, 4-methylcyclohexanone does not interact with other components to a greater extent, consequently the whole system tends towards an ideal behaviour. These findings are further confirmed by the results of Kendall-Munroe's relation and of Additive relation, both of which take into account ideal mixing of solutions. The standard percentage errors are better than those obtained with Frenkel's relation (Table 2).

Here it should be noted that Bingham's relation which gives the ideal viscosity of the mixture, fails to yield good results for systems III, IIIA, IIIB and IIIC (Table 2). This discrepancy is due to the fact that Bingham considered simple additivity of viscosities of component solutions, whereas the viscosity of mixtures follow the rule of logarithmic additivity. Simple additivity is also the cause for the absurd results obtained by Hind's relation (Table 2).

The ternary mixtures (IIID or IA), which does not contain 4-methylcyclohexanone, again follows the same trend with regard to standard percentage errors for Frenkel's, Kendall-Munroe's, Additive, Bingham's and Hind's relations as 9.05, 1.22, 6.61, 4.14 and 12.51 respectively.

Conclusion

Thus it is clear from the above discussion that Frenkel's relation gives the best results where interactions are involved whereas Kendall-Munroe's relation and Additive relation become more significant in the case of mixtures where an ideal mixing is expected. Bingham's relation and Hind's relation fail to provide any encouraging results as they do not follow the fundamental of logarithmic additivity. The results and trend of viscosities as calculated by various models clearly indicate that some properties of quaternary liquid mixtures are related to their constituent ternary liquid mixtures.

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