

Transport Studies of Multi-component Mixtures of Organic Liquids

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The theory of viscosity for liquid has been developed on the basis of Flory's statistical approach. Theoretical expressions obtained are applied to two quaternary and three ternary liquid systems. A comparative study and its correlation has been made on the basis of excess thermodynamic functions.

Key Words: Viscosity, Flory's statistical, Quaternary and ternary liquid systems.

INTRODUCTION

Viscous flow mechanism in multicomponent systems is of considerable physico-chemical interest in design calculations involving separation, heat transfer, mass transfer and fluid flow. Considerable amount of work has been done on binary¹⁻⁵ and ternary⁶ liquid mixtures. However, such studies are rare on quaternary systems except a few examples⁷.

The statistical thermodynamic study of transport properties is a direct consequence of molecular structure, specially size and shape of liquids and solutions. In the present work the statistical mechanical approach of Flory^{8,9} has been applied to multicomponent systems. It provides useful information in terms of different parameters, *i.e.*, lattice, distortion and disorder parameter^{10,11}, condensation effect¹², steric hindrance¹³⁻¹⁵, coupling of torsional oscillations¹⁶ and nature and extent of non-ideality¹⁷ parameter arising from the shape factor and molecular interaction.

EXPERIMENTAL

Component liquids were of AnalaR grade. They were purified and dried with the usual procedures¹⁸.

The systems prepared for the study were as given below:

Two quaternary systems: (1) Pentane-hexane-cyclohexane-benzene (2) Pentane-hexane-benzene-toluene.

Three ternary systems: (1) Pentane-hexane-benzene (2) hexane-cyclohexane-benzene (3) cyclohexane-heptane-toluene.

The viscosity measurements were carried out with a capillary viscometer at 298.15 ± 0.01 K.

RESULTS AND DISCUSSION

Theory

It is assumed that multi-component system can be considered to be made up from its contributory binaries. The molecules having f segments are divided into equal segments so that $v_1^* \dots v_f^* = v^*$. Assuming the additivity of core volumes of the components and adopting the same procedure as employed in case of binary mixtures, it is possible to evaluate the characteristic parameters of a multicomponent system.

Combining the, absolute reaction rate theory¹⁹ and the free volume theory²⁰⁻²² of liquid viscosity, one obtains²³, the expression for the viscosity of liquid mixtures,

$$\eta = A \exp \left[\frac{\Delta G^*}{RT} + \frac{\Upsilon V^*}{V_f} \right] \quad (1)$$

where ΔG^* is the free energy of activation per mole, R , the gas constant, V^* the enthalpy volume which must be available for a molecular segment jumping to its new site, V_f the free volume per segment in the mixture, Υ is a factor of order unity and η the viscosity of the liquid. Free energy of activation²³ in the case of, a multicomponent liquid system can be expressed as,

$$\Delta G = \left[\sum_{i=1}^f x_i \Delta G_i^* - \alpha \Delta G G_M^R \right] \quad (2)$$

where ΔG_M^R is the residual free energy of mixing and α is a constant of order unity.

The residual free energy of mixing can in term be broken into enthalpy and entropy contributions:

$$\Delta G_M^R = \Delta H_M - T \Delta S_M^R \quad (3)$$

where ΔH_M is the enthalpy of mixing per mole and ΔS_M^R the residual entropy of mixing per mole.

The residual free energy of mixing may be defined as

$$\Delta G_M^R = \Delta G_M - \Delta G_{\text{comb.}} \quad (4)$$

where ΔG_M is the free energy of mixing and $\Delta G_{\text{comb.}}$ the combinatorial free energy. Obviously, ΔG_M becomes identical with G^E , if $\Delta G_{\text{comb.}}$ be represented by the ideal mixing law.

The simplified form of the expression for residual free energy of mixing for a quaternary system is given as:

$$\Delta G_M^R = \left[\sum_{i=1}^f N_i P_i^* V_i^* \left(\frac{1}{\tilde{V}_i} - \frac{1}{\tilde{V}} \right) + 3\tilde{T}_i \ln \frac{(\tilde{v}_i^{1/3} - 1)}{(\tilde{v}^{1/3} - 1)} + \sum_{i=1}^f \sum_{j=f}^1 \left(\frac{N_i v_i^* \theta_{ij} x_{ij}}{\tilde{v}_i} \right) \right] \quad (5)$$

Molecular interaction study plays a vital role in elucidating the complete picture of the multicomponent system. Nature and extent of molecular interactions are generally expressed in terms of excess functions, *i.e.*, y^E and derived from the statistical equations of Flory and Gunberg-Nissan respectively. The value of the excess viscosity, η^E , has been evaluated using the following relation:

$$\eta^E = \eta_{\text{exp}} - \eta_{\text{id}}^i \quad (6)$$

where

$$\eta_{\text{id}} = \sum_{i=1}^f X_i \eta_i$$

Gunberg-Nissan equation for a multicomponent system can be expressed as

$$\ln \eta = \left[\sum_{i=1}^f X_i \ln \eta_i + (\sum X)_{1 \dots f} \varepsilon \right] \quad (7)$$

where ε is the measure of non-ideality parameter and is evaluated by the equation (7). Exhaustive study of non-ideality parameter and excess viscosity η^E reveals about the fate of interaction which seems to be weakened by the addition of the third and fourth components in multicomponent system which is supported by the work of Rastogi²⁴ and others^{25, 26}. According to Nigam and Dhillon²⁶, if $\varepsilon > 0$ and higher in magnitude there will be strong specific interaction in the mixture, and if $\varepsilon < 0$ weak interaction is indicated. The extent of interaction is expressed in terms of $\alpha \Delta F_m$ and w_{vis} . The interaction energy expression for $\alpha \Delta F_m$ and w_{vis} in the case of a multicomponent system can be written as

$$\alpha \Delta F_m = -RT(\ln \eta_{\text{theo.}} - \ln \eta_{\text{id.}}) \quad (8)$$

$$w_{\text{vis}} = \frac{RT}{\delta} \ln \frac{V}{\sum_{i=1}^f V_i X_i} + ERT \quad (9)$$

where

$$\delta = (\sum X)_{1 \dots f} \quad (10)$$

The values of excess free energy of mixing and interaction energy obtained using the above relations have been incorporated in Tables 1–5. Negative value of interaction energy and positive values of excess free energy of mixing indicate the weakening of interaction in multicomponent systems as evidenced by a careful perusal of Tables 1–5.

Molecular shape and size, condensation effect, steric hindrance contribution etc. can be explained in terms of $\ln \eta_{\text{exp.}}$, $\ln \eta_{\text{theo.}}$ and $(\Delta \ln \eta_{\text{exp.}} - \Delta \ln \eta_{\text{theo.}})$ factors which are listed in Tables 1–5. It was found that with the van der Waals' model for energy, the difference $(\Delta \ln \eta_{\text{exp.}} - \Delta \ln \eta_{\text{theo.}})$ is relatively small for mixtures of molecules not having a large size difference. However, for the system having a large difference, the difference $(\Delta \ln \eta_{\text{exp.}} - \Delta \ln \eta_{\text{theo.}})$ should be relatively large due to increasing function of the size difference. The value of $\Delta \ln \eta_{\text{theo.}}$ can be adjusted to $\Delta \ln \eta_{\text{exp.}}$ by adding a term $\ln \eta \Delta v^*$ given by

TABLE-1
 EXPERIMENTAL AND THEORETICAL VISCOSITIES, THEIR PERCENTAGE DEVIATIONS, EXCESS EXPERIMENTAL AND THEORETICAL
 VISCOSITIES, IDEAL VISCOSITIES, NON-IDEALITY PARAMETERS, EXCESS FREE ENERGY OF MIXING AND INTERACTION
 ENERGY FOR (PENTANE-HEXANE-CYCLOHEXANE-BENZENE) SYSTEMS AT 298.15 K

X_1	X_2	X_3	$\eta_{\text{expt.}}$	$\eta_{\text{theo.}}$	% Δ	η_{idl} ($\text{kg m}^{-1} \text{s}^{-1}$)	$E_{\eta_{\text{expt.}}}$	$E_{\eta_{\text{theo.}}}$	$E_{\text{theo.}}$	$\alpha \Delta F_M$ (theo.) (cal.)	$W_{\text{vis.}}$ (theo.) (cal.)
0.0488	0.1238	0.1831	0.4749	0.5053	-6.40	0.4971	-0.1222	-0.0918	-0.3636	102.42	-194.78
0.0658	0.1078	0.2036	0.4793	0.5175	-7.97	0.6015	-0.1222	-0.0480	-0.2780	89.11	-145.04
0.0813	0.0934	0.2238	0.4924	0.5181	-5.22	0.6059	-0.1135	-0.0878	-0.2727	92.74	-143.45
0.1006	0.0778	0.2430	0.6090	0.5160	-5.05	0.5160	-0.1178	-0.0930	-0.2741	98.17	-145.76
0.1180	0.0629	0.2615	0.4908	0.5155	-5.03	0.6122	-0.1214	-0.0967	-0.2721	101.35	-144.91
0.1243	0.0466	0.2842	0.5192	0.5241	-0.94	0.6216	-0.1024	-0.0975	-0.2655	101.07	-142.88
0.1410	0.1304	0.3129	0.4903	0.4923	-0.41	0.5980	-0.1077	-0.1057	-0.2170	115.23	-113.58
0.1560	0.1262	0.1513	0.4311	0.4415	-2.41	0.5458	-0.1147	-0.1043	-0.3398	125.64	-118.31
0.1285	0.1192	0.5888	0.5654	0.5754	-1.77	0.6877	-0.1223	-0.1123	-0.1835	105.62	-98.17
0.1537	0.0925	0.1685	0.4593	0.4582	0.20	0.5621	-0.1028	-0.1039	-0.3414	121.08	-184.24
0.1649	0.1013	0.5177	0.5282	0.5383	-1.91	0.6582	-0.1300	-0.1199	-0.2051	119.13	-110.07
0.1368	0.1258	0.1507	0.4493	0.4520	-0.60	0.5532	-0.1039	-0.1012	-0.3392	119.69	-181.16
0.0910	0.1721	0.6137	0.5780	0.5861	-1.40	0.6932	-0.1152	-0.1071	-0.1678	99.42	-88.23
0.0649	0.1378	0.1103	0.4783	0.4828	-0.94	0.5651	-0.0868	-0.0823	-0.3589	93.25	-186.24
0.1810	0.1656	0.2971	0.4500	0.4497	-0.07	0.5674	-0.1177	-0.1174	-0.2840	137.73	-154.45

TABLE-2
 EXPERIMENTAL AND THEORETICAL VISCOSITIES, THEIR PERCENTAGE DEVIATIONS, EXCESS EXPERIMENTAL AND THEORETICAL
 VISCOSITIES, IDEAL VISCOSITIES, NON-IDEALITY PARAMETERS, EXCESS FREE ENERGY OF MIXING AND INTERACTION
 ENERGY FOR (PENTANE-HEXANE-BENZENE-TOLUENE) SYSTEMS AT 298.15 K

X ₁	X ₂	X ₃	$\eta_{\text{expt.}}$	$\eta_{\text{theo.}}$	% Δ	η_{idl} (kg m ⁻¹ s ⁻¹)	$\eta_{\text{expt.}}^E$	$\eta_{\text{theo.}}^E$	$\epsilon_{\text{theo.}}$	$\alpha \Delta F_M$ (theo.) (cal.)	$W_{\text{vis.}}$ (theo.) (cal.)
0.0943	0.0918	0.4587	0.4692	0.4442	5.33	0.5198	-0.0506	-0.0756	-0.3090	93.11	-168.84
0.1300	0.1373	0.2974	0.4283	0.4126	3.66	0.4887	-0.0604	-0.0761	-0.2816	100.28	-153.99
0.1278	0.1288	0.3589	0.4518	0.4611	-2.06	0.4943	-0.4250	-0.0732	-0.0296	41.19	-3.90
0.1450	0.1291	0.3376	0.4431	0.4534	-2.32	0.4875	-0.0444	-0.0341	-0.0264	42.96	-2.46
0.1492	0.1384	0.3421	0.4132	0.4038	2.27	0.4888	-0.0707	-0.0800	-0.2880	107.08	-157.16
0.1843	0.1484	0.2711	0.4052	0.3823	5.65	0.4062	-0.0610	-0.0839	-0.3068	117.54	-168.78
0.1823	0.1640	0.3613	0.3912	0.3791	3.09	0.4075	-0.0763	-0.0884	-0.3157	124.17	-181.12
0.1819	0.1606	0.3842	0.3992	0.3870	3.05	0.4891	-0.0699	-0.0821	-0.2808	113.98	-154.94
0.1250	0.1665	0.2455	0.4123	0.4038	2.06	0.4805	-0.0682	-0.0767	-0.2924	103.03	-160.54
0.1691	0.2041	0.2218	0.3810	0.3720	2.36	0.4546	-0.0736	-0.0826	-0.3102	118.79	-171.29
0.1866	0.0826	0.2250	0.3893	0.3953	-1.54	0.4763	-0.0870	-0.0810	-0.3808	110.43	-216.72
0.1372	0.1580	0.5548	0.4035	0.4106	-1.76	0.4921	-0.0886	-0.0815	-0.3250	107.26	-185.45
0.0660	0.1053	0.7033	0.5366	0.4768	-3.69	0.5366	-0.7680	-0.0598	-0.2998	69.99	-155.09
0.0524	0.1434	0.4201	0.4493	0.4594	-2.25	0.5187	-0.0696	-0.0593	-0.2238	71.92	-116.77
0.1568	0.0468	0.4582	0.4223	0.4347	-2.94	0.5103	-0.0780	-0.0756	-0.2847	94.99	-155.46

TABLE-3
 EXPERIMENTAL AND THEORETICAL VISCOSITIES, THEIR PERCENTAGE DEVIATIONS, EXCESS EXPERIMENTAL AND THEORETICAL VISCOSITIES, IDEAL VISCOSITIES, NON-IDEALITY PARAMETERS, EXCESS FREE ENERGY OF MIXING AND INTERACTION ENERGY FOR (PENTANE-HEXANE-BENZENE) SYSTEM AT 298.15 K

X_1	X_2	$\eta_{\text{expt.}}$	$\eta_{\text{theo.}}$	% Δ	η_{idl} ($\text{kg m}^{-1} \text{s}^{-1}$)	$\eta_{\text{expt.}}$	$\eta_{\text{theo.}}$	$E_{\text{theo.}}$	$\eta_{\text{theo.}}$	$\alpha \Delta F_M$ (theo.) (cal.)	$W_{\text{vis.}}$ (theo.) (cal.)
0.0966	0.4171	0.3863	0.3946	-2.15	0.4351	-0.0488	-0.0405	-0.0617	57.88	-20.01	
0.1429	0.3739	0.3802	0.3875	-1.92	0.4306	-0.0504	-0.0431	-0.0751	68.40	-27.74	
0.2017	0.3388	0.3723	0.3786	-1.69	0.4188	-0.0465	-0.0402	-0.0379	59.78	-43.66	
0.2590	0.3039	0.3553	0.3549	0.11	0.4766	-0.1153	-0.1157	-0.1239	107.16	-68.67	
0.2985	0.2877	0.3297	0.3387	2.73	0.3974	-0.0677	-0.0587	-0.1720	94.68	-87.84	
0.3075	0.2946	0.3253	0.3295	-1.29	0.3919	-0.0666	-0.0624	-0.2678	102.74	-107.47	
0.3426	0.3143	0.3221	0.3244	-0.71	0.3727	-0.0506	0.0483	-0.1151	82.23	-57.37	
0.3686	0.3423	0.3098	0.3169	-2.29	0.3509	-0.0411	-0.0340	-0.0321	60.38	-12.26	
0.4099	0.3888	0.3199	0.3243	-1.37	0.3238	-0.0039	0.0005	0.2249	-0.91	128.39	
0.4082	0.4665	0.3001	0.3037	-1.20	0.3008	-0.0007	0.0029	0.2078	-5.68	118.23	

TABLE-4
 EXPERIMENTAL AND THEORETICAL VISCOSITIES, THEIR PERCENTAGE DEVIATIONS, EXCESS EXPERIMENTAL AND THEORETICAL
 VISCOSITIES, IDEAL VISCOSITIES, NON-IDEALITY PARAMETERS, EXCESS FREE ENERGY OF MIXING AND INTERACTION ENERGY FOR
 (HEXANE-CYCLOHEXANE-BENZENE) SYSTEM AT 298.15 K

X_1	X_2	$\eta_{\text{expt.}}$	$\eta_{\text{theo.}}$	% Δ	η_{idl} ($\text{kg m}^{-1} \text{s}^{-1}$)	$\eta_{\text{expt.}}^E$	$\eta_{\text{theo.}}^E$	$\eta_{\text{theo.}}^E$	$\alpha \Delta F_M$ (theo.) (cal.)	$W_{\text{vis.}}$ (theo.) (cal.)
0.0771	0.4315	0.6253	0.6654	-6.41	0.7034	-0.0781	-0.0380	-0.0454	32.90	-14.80
0.1269	0.4150	0.5923	0.6110	-3.16	0.6833	-0.0910	-0.0723	-0.1747	66.25	-85.88
0.1795	0.3854	0.5889	0.5960	-1.20	0.6584	-0.0695	-0.0624	-0.0939	58.99	-39.90
0.2279	0.3501	0.5595	0.5645	-0.80	0.6332	-0.0737	-0.0687	-0.1063	68.04	-46.25
0.2616	0.3342	0.5632	0.5738	-1.88	0.6183	-0.0551	-0.0445	-0.0239	44.25	24.98
0.2812	0.3348	0.5239	0.5475	-4.50	0.6125	-0.0886	-0.0650	-0.0665	66.46	-24.97
0.3021	0.3643	0.5521	0.5629	-1.77	0.6147	-0.0616	-0.0518	-0.0171	52.15	21.07
0.3062	0.3823	0.5423	0.5553	-2.40	0.6188	-0.0765	-0.0635	-0.0312	64.14	-6.83
0.3448	0.4567	0.5608	0.5966	-6.38	0.6290	-0.0682	-0.0294	0.0112	31.33	8.12
0.3231	0.4857	0.5598	0.5883	-5.09	0.6440	-0.0842	-0.0557	0.0497	53.59	36.28

TABLE-4
 EXPERIMENTAL AND THEORETICAL VISCOSITIES, THEIR PERCENTAGE DEVIATIONS, EXCESS EXPERIMENTAL AND THEORETICAL
 VISCOSITIES, IDEAL VISCOSITIES, NON-IDEALITY PARAMETERS, EXCESS FREE ENERGY OF MIXING AND INTERACTION ENERGY FOR
 (CYCLOHEXANE-HEPTANE-TOLUENE) SYSTEM AT 298.15 K

X_1	X_2	$\eta_{\text{expt.}}$	$\eta_{\text{theo.}}$	% Δ	η_{lid} ($\text{kg m}^{-1} \text{s}^{-1}$)	$\eta_{\text{E}}^{\text{E}}$	$\eta_{\text{theo.}}^{\text{E}}$	$\eta_{\text{theo.}}$	$\alpha \Delta F_M$ (theo.) (cal.)	$W_{\text{vis.}}$ (theo.) (cal.)
0.1124	0.3962	0.6845	0.7501	-9.58	0.5266	-0.1579	-0.2235	1.2350	-209.58	706.62
0.1761	0.3766	0.6523	0.6992	-7.19	0.5515	-0.1008	-0.1477	0.8243	-140.58	475.09
0.2452	0.3379	0.6743	0.7104	-5.35	0.5815	-0.0928	-0.1289	0.6983	-118.61	704.03
0.3027	0.3032	0.6789	0.7129	-5.01	0.6069	-0.0726	-0.1060	0.5871	-95.37	340.13
0.3480	0.2837	0.7231	0.7530	-4.13	0.6256	-0.0975	-0.1274	0.6564	-109.81	378.23
0.3760	0.2896	0.7293	0.7637	-4.72	0.6341	-0.0952	-0.1296	0.6641	-110.17	382.62
0.3908	0.3050	0.7573	0.7885	-4.12	0.6365	-0.1208	-0.1520	0.7485	-126.87	428.10
0.4198	0.3417	0.7598	0.7888	-3.82	0.6401	-0.1197	-0.1487	0.7646	-123.75	440.10
0.4668	0.3797	0.8023	0.8448	-5.30	0.6428	-0.1595	-0.2020	1.0053	-161.89	575.63
0.4526	0.4393	0.7999	0.8322	-4.04	0.6347	-0.1652	-0.1975	1.1014	-160.50	630.91

$$\ln \eta \Delta v^* = \left[\sum_{i=1}^f \sum_{j=f}^1 c_{ij} (v_i^{*1/2} - v_j^{*1/2})^2 \right]; \quad i \neq j \quad (11)$$

where v^* is the core volume and c_{ij} is the adjustable parameter. On the basis of the above fact, it can be concluded that the molecules constituting the system have moderately small size difference due to low magnitude of the values.

The size effect makes the shape effect too. It is very much possible that the liquid viscosity is increased when the molecules have a large size difference, because the probability of a suitable empty site near the molecules diminishes. This is likely due to good filling of the small molecules in between the space left by the large ones and it may be the only reason for the increased viscosity and decreased volume³¹. Thus, the structural orientations and shapes of the molecules are altered completely.

The condensation effect is related to some kind of couplage between the motions of the condensing and condensed v molecules. If the molecules have the same shape, it is possible that the maximum of the effect does not happen.

Steric hindrance contribution is associated with the difference between the experimental and theoretical excess data. Significant steric hindrance contribution is supposed to occur either when a molecule in the mixture was a crowded central atom, such as the highly branched alkanes or when it has a special flat shape as cyclopentane.

A careful perusal of Table 3 and 4 shows that reasonable agreement has been achieved between theory and experiment which proves the validity of statistical mechanical theory of Flory. The average percentage deviation has been found to be +2.69, ± 2.93 , ± 1.55 , ± 3.37 and ± 5.32 , respectively. The results obtained from the Flory's statistical theory can be improved further by considering three and four body effects also. In defining the segment and site fractions, a spherical shape of molecule, *i.e.*, the minimum area of contact has been assumed. The possibility of only two body interactions has been considered during the extension of the theory. However, there is every possibility of three and four body interactions also, and these have been ignored in order to simplify the theoretical procedure. Although three and four body interactions contribute very little to the energy of the system, they probably cannot be ignored in spite of the spherical nature of the molecules. The possibility of the three and four body collisions increases as the chain length increases, *i.e.*, the area of contact increases. Therefore, in order to get comparable results, a correction term is needed to include three and four body effects in the evaluation of characteristic and interaction energy parameters.

ACKNOWLEDGEMENT

The authors are thankful to Dr. U.S. Pandey, Retired Professor and Head of department of chemistry, Veer Kunwar Singh University, Ara for his valuable suggestions and keen interest during the work.

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(Received: 22 February 2003; Accepted: 30 July 2003)

AJC-3143