Temperature dependent study of viscosity of KNO$_3$-NaNO$_2$-NaNO$_3$ ternary molten salts

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Temperature dependent study of viscosity has been employed for KNO_3–$NaNO_2$–$NaNO_3$ ternary molten salts using various empirical and statistical theories. The values derived are found to be in a fairly good agreement with the experimental values reported in the literature. Thus, the theories can be validated for its application to the multicomponent systems in general.

Keywords: Molten salts; Ternary mixtures; Viscosity

1. Introduction

Various empirical relations and Flory's statistical theory [1,2] were developed and applied by various workers [3–5] for studying the viscous behaviour of binary liquid mixtures. The estimation of viscosity and thermodynamic activation parameters for these binary systems is helpful in assessing the molecular size and shape [6–9], contribution to steric hinderance [6,10,13], coupling of tortional oscillations [14] and extent of non-ideal behaviour [15,16]. The latter, in fact, depends on the molecular structure [18] and intermolecular interactions in different combinations. However, the applicability and execution of these theories for viscosity of multicomponent systems are very rare, despite its application in chemical engineering [18,19] e.g. design calculations for heat transfer, mass transfer and fluid flow etc., which are immensely important and provide a basis for the selection of a physicochemical method of analysis, especially in the field of petrochemical and drug industry. Very recently [20–24], measurement of viscosities has been carried out successfully, but the theoretical interpretations have not been carried out till now as far as our knowledge is concerned. Since the experimental determination of viscosity at elevated temperature is very rare, its theoretical applicability could not be done earlier. A comparative study of various theories has been made from the work of Gaune [25] over a wide range of temperatures in the present context.

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2. Theoretical

Recently, various empirical relations namely Frankel, Kendall–Munrae, Additive, Bingham and Hind–Ubbelhode were extended for ternary systems.

$$\eta = \sum_{i=1}^{i=3} X_i \eta_i \tag{1}$$

where, X_i and η_i are the mole fractions and viscosities of pure components respectively.

$$\ln \eta = \sum_{i=1}^{i=3} X_i \ln \eta_i \tag{2}$$

$$\ln \eta v = \sum_{i=1}^{i=3} \ln \eta_i \ V_i \tag{3}$$

$$\begin{aligned}
\ln \eta v = {}& x_1^2 \ln \eta_1 + x_2^2 \ln \eta_2 + x_3^2 \ln \eta_3 \\
& + 2(x_1 x_2 \ln \eta_{12} + x_1 x_3 \ln \eta_{13} + x_2 x_3 \ln \eta_{23}) \\
& + 3 x_1 x_2 x_3 \ln \eta_{123}
\end{aligned} \tag{4}$$

Considering the possibility of two body interactions, the statistical mechanical approach of Flory has been used to develop an expression for the dynamic viscosity of a ternary liquid mixture, using the concept of absolute rate and free volume theories of liquid state, and the following equations have been obtained.

$$\ln \eta = \sum_{i=1}^{i=3} x_i \ln \eta_i \& \frac{\Delta G_M^R}{RT} + \frac{1}{\tilde{V}-1} \& \sum_{i=1}^{i=3} \frac{x_i}{\tilde{V}_i - 1} \tag{5}$$

The residual free energy of mixing, G_M^R is generally expressed by the relation,

$$\Delta G_M^R = \Delta H_M^R - T \Delta S_M^R \tag{6}$$

where, ΔH_M^R is the enthalpy of mixing per mole. It takes the following form for a ternary system.

$$\Delta H_M^R = \sum_{i=1}^{i=3} x_i P_i^* V_i^* \left(\frac{1}{\tilde{V}_i} - \frac{1}{\tilde{V}} \right) + \frac{x_1 V_1^* \theta_2 X_{12}}{\tilde{V}_1} + \frac{x_2 V_2^* \theta_3 X_{23}}{\tilde{V}_2} + \frac{x_3 V_3^* \theta_1 X_{31}}{\tilde{V}_3} \tag{7}$$

Viscous behaviour cannot be explained on the basis of free volume effects only, but residual entropy of mixing has been considered to act as a major additional factor of activation flow. The value of residual entropy of mixing can be evaluated using the following expression:

$$\Delta G_M^R = - \sum_{i=1}^{i=3} \left[\frac{3 x_i P_i^* V_i^* \tilde{T}_i}{T} \ln \frac{(\tilde{V}_i^{1/3} - 1)}{(\tilde{V}^{1/3} - 1)} \right] \tag{8}$$

With the help of equations (5)–(8) we can get the following expression for the viscosity of ternary mixtures.

$$
\begin{aligned}
\ln \eta = {} & x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_3 \ln \eta_3 \Bigg[-x_1 P_1^* V_1^* \left\{ \left(\frac{1}{V_1} - \frac{1}{V} \right) \right. \\
& + 3T_1 \ln \frac{(V_1^{1/3} - 1)}{(V^{1/3} - 1)} \Bigg\} + x_2 P_2^* V_2^* \left\{ \left(\frac{1}{V_2} - \frac{1}{V} \right) + 3T_2 \ln \frac{(V_1^{1/3} - 1)}{(V^{1/3} - 1)} \right\} \\
& + x_3 P_3^* V_3^* \left\{ \left(\frac{1}{V_3} - \frac{1}{V} \right) + 3T_3 \ln \frac{(V_3^{1/3} - 1)}{(V^{1/3} - 1)} \right\} \\
& + \frac{x_i V_1^* \theta_2 X_{12}}{V_1} + \frac{x_2 V_2^* \theta_3 X_{23}}{V_2} + \frac{x_3 V_3^* \theta_1 X_{31}}{V_3} \Bigg] \\
& + \frac{1}{V-1} - \left(\frac{x_1}{V_1 - 1} + \frac{x_2}{V_2 - 1} + \frac{x_3}{V_3 - 1} \right)
\end{aligned}
\tag{9}
$$

All the notations in the above equations have their usual significance and their evaluation has been detailed out in our earlier papers [26,27]. All the possible interchange energy parameters x_{12}, x_{23} and x_{31} have been considered. The possibility of three body interactions is ignored in order to make the theory simple. The interchange energy parameters can be evaluated using the following general expression.

$$
x_{ij_{i \neq j}} = P_i^* \left[1 - \left(\frac{P_j^*}{P_i^*} \right)^{1/2} \left(\frac{V_j^*}{V_i^*} \right)^{1/6} \right]^2
\tag{10}
$$

3. Results and discussion

The viscosities of $KNO_3(X_1) + NaNO_2(X_2) + NaNO_3(X_3)$ ternary system at two compositions have been computed over a wide range temperature using Bingham (Bing), Kendall–Munrol (KM), Additive (Add), Frenkel (Frenk) and Flory's statistical theory. The values of viscosities and molar volume of the pure components are taken from the literature [29,30] for the temperature range in which values are available. The values at the rest of the temperatures are determined by graphical extrapolation and are recorded in tables 1 and 2 for the compositions 1 and 2 respectively.

The viscosities of ternary mixture compositions 1 and 2 are shown in tables 3 and 4 respectively. The standard percentage of errors for the Bing, KM, Add and Frenk are 9.32, 9.72, 10.05 and 12.38 respectively. Similar trend is also obtained at composition 2, in which the standard percentage errors by all the relations are 11.79, 11.73, 11.19 and 15.97, respectively.

The standard percentage errors obtained by Flory's statistical theory for compositions 1 and 2 are 8.716 and 20.68, respectively. It is observed that the results at composition 1 are fairly good but are not very encouraging at composition 2. This is in consistence with the finding that the addition of a third component weakens the interactions. Since the density values have been extrapolated because of the non-availability of data, all temperatures are responsible since α is very sensitive to even small temperature variations and hence, to some extent, the deviation may also be due to the extrapolated values of the coefficient of thermal expansion.

Table 1. Parameters of the pure components at varying temperatures for ($x_1 = 0.4396$, $x_2 = 4158$).

S. no.	Temperature (K)	$\alpha_1 \times 10^4$ (K^{-1})	$\alpha_2 \times 10^4$ (K^{-1})	$\alpha_3 \times 10^4$ (K^{-1})	$\beta_{T_1} \times 10^6$ (KPa^{-1})	$\beta_{T_2} \times 10^6$ (KPa^{-1})	$\beta_{T_3} \times 10^6$ (KPa^{-1})	ρ_1 (gcc^{-1})	ρ_2 (gcc^{-1})	ρ_3 (gcc^{-1})
1	489	3.7222	3.6287	4.0082	0.1035	0.1000	0.0983	1.95852	1.86121	1.97037
2	527	3.7756	3.6795	4.0701	0.1068	0.1019	0.0966	1.93082	1.83286	194320
3	599	3.8811	3.7796	4.1930	0.1136	0.1056	0.1022	1.87833	1.77915	1.89172
4	622	3.9161	3.8128	4.2339	0.1159	0.1069	0.1419	1.86156	1.76199	1.87527
5	655	3.9673	3.8614	4.2938	0.1193	0.1087	0.1042	1.83751	1.73737	1.85168
6	716	4.0157	3.9545	4.4093	0.1262	0.1122	0.1066	1.79304	1.69186	1.80806
7	753	4.1278	4.0132	4.4825	0.1307	0.1144	0.1080	1.76606	1.66426	1.78161
8	755	4.1312	4.0165	4.4865	0.1309	0.1145	0.1081	1.76461	1.66277	1.78018

Table 2. Parameters of the pure components at varying temperatures for ($x_1 = 0.4421$, $x_2 = 4885$).

S. no.	Temperature (K)	$\alpha_1 \times 10^4$ (K^{-1})	$\alpha_2 \times 10^4$ (K^{-1})	$\alpha_3 \times 10^4$ (K^{-1})	$\beta_{T_1} \times 10^6$ (KPa^{-1})	$\beta_{T_2} \times 10^6$ (KPa^{-1})	$\beta_{T_3} \times 10^6$ (KPa^{-1})	ρ_1 (gcc^{-1})	ρ_2 (gcc^{-1})	ρ_3 (gcc^{-1})
1	457	3.6783	3.5871	3.9574	0.1008	0.0972	0.0985	1.98185	1.88508	1.99325
2	459	3.6811	3.5896	3.9605	0.1010	0.0973	0.0986	1.98039	1.88359	1.99182
3	481	3.7112	3.6182	3.9953	0.1028	0.0903	0.0996	1.96435	1.86797	1.97609
4	513	3.7557	3.6606	4.0471	0.1055	0.0991	0.1012	1.94102	1.84330	1.95321
5	528	3.7770	3.6809	4.0718	0.1069	0.0996	0.1019	1.93009	1.83211	1.94248
6	575	3.8453	0.7457	4.1512	0.1112	0.1013	0.1044	1.8958	1.79705	1.90887
7	591	3.8691	3.7682	4.1790	0.1128	0.1019	0.1052	1.88416	1.78511	1.89744
8	646	3.9532	3.6479	4.2773	0.114	0.1039	0.1082	1.84407	1.74408	1.85811
9	673	3.9958	3.8884	4.3373	0.1213	0.1049	0.1097	1.82438	1.72394	1.83881
10	698	4.0362	3.9265	4.3746	0.1241	0.1059	0.1111	1.80616	1.70529	1.82093
11	755	4.1312	4.0165	4.4865	0.1309	0.1081	0.1145	1.76461	1.66277	1.78018
12	785	4.1831	4.0654	4.4577	0.1348	0.1093	0.1164	1.74274	1.64039	1.75872
13	789	4.1901	4.0721	4.5560	0.1353	0.1095	0.1167	1.73982	1.63741	1.75581
14	792	4.1954	4.0770	4.5622	0.1357	0.1096	0.1168	1.73762	1.63517	1.72372

Table 3. Comparison between theoretical and observed viscosity values of ternary liquid melt ($KNO_3 + NaNO_2 + NaNO_3$) at varying temperatures.

S. no	Temperature (K)	η_{exp}(cP)	η_{Bing} (cP)	η_{KM} (cP)	η_{Add}(cP)	η_{Frenk} (cP)	η_{eFlory} (cP)	Δ%				
								Bing	KM	Add	Frenk	Flory
1	489	5.275	4.716	4.723	4.664	5.342	4.840	10.59	10.46	11.58	−1.27	8.25
2	527	3.869	3.843	3.807	3.794	4.275	3.881	0.67	1.60	1.94	−10.49	−0.31
3	599	2.505	2.700	2.690	2.658	2.915	2.634	−7.78	−7.38	−6.12	−16.37	−9.14
4	622	2.180	2.392	2.379	2.351	2.621	2.419	−9.72	−9.13	7.84	−20.23	−1.96
5	655	1.915	2.021	2.003	1.979	2.128	2.042	−5.53	−4.59	−3.34	−11.12	−6.63
6	716	1.585	1.496	1.479	1.462	1.538	1.521	5.62	6.69	7.76	2.97	4.40
7	753	1.442	1.263	1.239	1.225	1.277	1.284	12.41	14.08	15.05	11.44	10.96
8	755	1.460	1.248	1.233	1.219	1.268	1.278	14.52	15.55	16.51	13.15	12.47
						Mean percentage deviation=		8.355	8.701	8.767	10.880	7.845
						Standard percentage error=		9.318	9.719	10.045	12.375	8.716

Table 4. Comparison between theoretical and observed viscosity values of ternary liquid mixture ($KNO_3 + NaNO_2 + NaNO_3$) at varying temperatures.

S. no	Temperature (K)	ηexp (cP)	ηBing (cP)	ηKM (cP)	ηAdd (cP)	ηFrenk (cP)	ηFlory (cP)	Δ%				
								Bing	KM	Add	Frenk	Flory
1	457	6.205	6.215	6.215	6.152	6.746	7.231	−0.16	0.16	0.85	−8.70	−16.50
2	459	6.372	6.010	6.010	5.949	6.514	6.981	0.06	0.06	0.07	−2.20	−9.50
3	481	4.755	4.924	4.923	4.873	5.289	5.676	−3.60	−3.50	−2.50	−11.20	−19.40
4	513	3.911	4.109	4.107	4.067	4.377	4.681	−5.10	−5.01	−3.99	−11.90	−19.70
5	528	3.261	3.803	3.801	3.764	4.036	4.039	−16.62	−16.55	−15.43	−23.71	32.13
6	575	2.569	3.024	3.018	2.990	3.176	3.369	−17.71	−17.48	−16.38	−23.62	−31.10
7	591	2.217	2.713	2.784	2.759	2.999	3.091	−25.98	−25.57	−24.45	−35.27	−39.41
8	646	1.868	2.092	2.073	2.055	2.154	2.260	−11.99	−10.97	−10.01	−15.31	−20.98
9	673	1.591	1.803	1.783	1.768	1.843	1.924	−13.32	−12.06	−11.12	−15.84	−20.93
10	698	1.408	1.568	1.548	1.535	1.592	1.656	−11.36	−9.94	−9.02	−13.07	−17.61
11	755	1.209	1.226	1.202	1.192	1.227	1.257	−1.41	0.01	−1.49	−1.49	−3.97
12	785	1.218	1.121	1.100	1.091	1.118	1.189	7.96	9.69	10.42	8.21	2.38
13	789	1.231	1.106	1.078	1.077	1.103	1.110	10.15	12.40	12.51	10.39	9.82
14	792	1.143	1.086	1.067	1.059	1.083	1.151	4.99	6.65	7.35	5.25	−0.01
						Mean percentage deviation =		9.32	9.29	8.97	13.29	17.39
						Standard percentage error =		11.79	11.73	11.19	15.97	20.68

The nature and extent have been the study terms of various interaction parameters, which are tabulated in tables 5 and 6 for compositions 1 and 2 respectively. These parameters explain the nature and extent of the molecular interactions involved using the concept of Flory's theory, considering two body interactions only and the concept of Grunberg and Nissan [31] in terms of ε where all possible interactions occur.

The values of excess free energy of mixing ($\alpha\Delta F_m$) and interaction energy (W_{vis}) have also been recorded, which appear to be liable for the shape and size of the molecules in the ternary system.

The excess viscosity η^ε, can be evaluated using the following relations:

$$\eta^\varepsilon_{exp} = \eta_{exp} - \eta_{id} \tag{11}$$

and

$$\eta^\varepsilon_{Theo} = \eta_{Theo} - \eta_{id} \tag{12}$$

where

$$\eta_{id} = \sum_{i=1}^{i=3} x_i\eta_i$$

Table 5. Excess viscosity and interaction parameters of the system ($KNO_3 + NaNO_2 + NaNO_3$) at varying temperatures.

S. no.	Temperature (K)	η_{exp} (cP)	η^ε	η_{Theo1}	η_{Theo2}	ε	$\alpha\,\Delta F_m \times 10^3$ (J mol^{-1})	$W_{vis} \times 10^3$ (J mol^{-1})
1	489	5.275	0.559	0.007	0.124	0.47645	14.7900	2.11102
2	527	3.869	0.026	0.036	0.038	0.06963	20.2245	0.48792
3	599	2.505	0.195	0.010	0.034	−0.30713	21.7861	−1.33290
4	622	2.180	−0.212	−0.013	0.027	−0.37654	23.1870	−1.74690
5	655	1.915	−0.106	−0.018	0.021	−0.19366	24.8663	−0.84969
6	716	1.585	0.089	−0.017	0.025	0.29836	24.3536	1.98730
7	753	1.442	0.179	−0.024	−0.021	0.65401	25.6471	4.30809
8	755	1.460	0.212	−0.015	0.030	0.72841	23.4015	4.78608

Table 6. Excess viscosity and interaction parameters of the system ($KNO_3 + NaNO_2 + NaNO_3$) at varying temperatures.

S. no	Temperature (K)	η_{exp} (cP)	η^ε	η_{theo1}	η_{theo2}	ε	$\alpha\,\Delta F_m \times 10^3$ (J mol^{-1})	$W_{vis} \times 10^3$ (J mol^{-1})
1	457	6.205	−0.010	0.0	1.015	−0.00694	6.8841	0.14005
2	459	6.372	0.362	0.0	0.97	0.25211	6.9599	1.12902
3	481	4.755	−0.169	−0.001	0.752	−0.14966	7.5146	−0.42609
4	513	3.911	−0.198	−0.002	0.572	−0.21078	8.4097	−0.71919
5	528	3.261	−0.542	−0.002	0.506	−0.66049	8.8526	−2.71588
6	575	2.569	−0.455	−0.006	0.345	−0.69431	10.3774	−3.12670
7	591	2.217	−0.576	−0.009	0.298	−0.98163	10.9942	−4.62750
8	646	1.868	−0.224	−0.019	0.168	−0.44884	13.5446	−2.20704
9	673	1.591	−0.212	−0.020	0.121	−0.49111	15.1144	−2.54070
10	698	1.408	−0.160	−0.020	0.088	−0.40860	16.7139	−2.16140
11	755	1.209	−0.017	−0.024	0.031	0.02503	23.0841	0.37093
12	785	1.218	0.097	0.021	0.068	0.43923	18.2889	3.08151
13	789	1.231	0.125	0.028	0.004	0.57208	36.8761	3.96730
14	792	1.143	0.057	−0.019	0.065	0.29658	18.5396	2.16792

Magnitude of η_{exp}^{ε} shows actual deviation of the system from the ideal behaviour. A close perusal of tables 5 and 6 shows a larger variation by Flory's theory, which is due to the fact that only two body interactions have been the considerations and the possibility of three body interactions has not been taken into account. In electrolytic solutions interionic attractions and interactions between similar components are also not considered.

Gunberg–Nissan equation includes all possible interactions and enables the evaluation of the non-ideal parameter ε. The equation can be represented as

$$\ln \eta = \sum_{i=1}^{i=3} x_i \ln \eta_i + \varepsilon(x_1 x_2 + x_2 x_3 + x_3 x_1 + x_1 x_2 x_3) \tag{13}$$

where ε is the measure of non-ideality. According to Nigam *et al.* [32] $\varepsilon > 0$ and higher magnitude of these values at both the compositions shows weak interactions, but these interactions tend to increase at very low and very high temperatures which is indicated by a small positive value of ε.

The values of excess free energy of mixing ($\alpha \Delta F_m$) and interaction energy (W_{vis}) are evaluated by the following equation

$$\alpha \Delta F_m = -RT(\ln \eta_{Theo} - \ln \eta_{id}) \tag{14}$$

Negative value of interaction energy and positive values of excess free energy of mixing indicate weak interactions. These weak interactions at both the compositions are confirmed by the positive values of $\alpha \Delta F_m$, which vary from $6.88 \times 10^3 \, \text{J mol}^{-1}$ to $36.88 \times 10^3 \, \text{J mol}^{-1}$. (This is due to the fact that, both at lower and higher temperatures, ionic interactions exist.)

Acknowledgement

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