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Viscosity of the systems *m*-xylene, +1-propanol, +2-propanol, +1-butanol, +*t*-butanol

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Viscosities, η , of the systems, *m*-xylene, +1-propanol, +2-propanol, +1-butanol and +*t*-butanol have been measured for the whole range of composition at 303.15, 308.15, 313.15, 318.15 and 323.15 K. The variation of viscosities has been plotted against mole fraction of alkanols. Viscosities have been found to increase slowly up to a considerable concentration of alkanols, followed by a rapid rise of viscosities at higher concentrations. The slow rise of viscosity is attributed to dissociation of alkanols in *m*-xylene, while the rapid rise of viscosity is ascribed to self-association of alkanols. Excess viscosities, $\eta^{\rm E}$, have been plotted as a function of mole fraction of alkanols. The curves show negative values for the whole range of composition, with minima occurring in alkanol-rich region. η and $\eta^{\rm E}$ have been fitted to appropriate polynomial equations. The study shows the effect of branching and chain length of alkanols on η and $\eta^{\rm E}$.

Keywords: Viscosity; m-Xylene; 1-Propanol; 2-Propanol; 1-Butanol; t-Butanol

1. Introduction

This is a part of our ongoing research on volumetric and viscometric properties of binary liquid mixtures with the objective of understanding homo- and heteromolecular interaction in liquid systems. Although a good number of studies on viscometric properties of the solutions of xylenes with a variety of organic liquids are available, we are not aware of any viscometric study on the mixtures of xylenes and alkanols. This prompted us to undertake a study on the viscometric xylenes + alkanols.However, properties of there exist some viscometric studies on toluene + alkanols in literature, of which the works of Akhtar *et al.* [1]and Nikam et al. [2] are considered very useful in connection with our work. We report here the viscometric properties of *m*-xylene+isomers of alkanols

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containing three and four carbon atoms, with the intention to see the effect of branching as well as chain length of alkanols.

2. Experimental

Chemicals used for this investigation have been procured from Aldrich with quoted purities: 1-propanol (99.5%), 2-propanol (99.5%), 1-butanol (99.8%), *t*-butanol (99.5%) and *m*-xylene (99+%). These have been used without any further treatment, except that alkanols were kept over molecular sieves (4A) for at least three weeks prior to their use.

The density was measured by a 25 mL specific gravity bottle previously calibrated with redistilled water. An analytical balance weighing up to ± 0.0001 g was used in the density measurement. The same balance was used to make solutions, the calculated mole fractions were accurate up to the fourth place of decimal. Temperature was controlled by a thermostatic water bath with the fluctuation of ± 0.05 K. The average uncertainty in the measured density was 1.4×10^{-1} kg m⁻³.

An Ostwald U-tube viscometer (British Standard Institution), with sufficiently long efflux time, was used so that no kinetic energy correction was necessary in viscosity measurement. The viscometer was calibrated earlier by redistilled water. The time of flow was recorded by a timer accurate up to ± 0.1 s. The average uncertainty in the measured viscosity was estimated to be less than 6×10^{-7} kg m⁻¹ s⁻¹.

3. Results and discussion

Table 1 shows the densities and viscosities of the pure compounds, *m*-xylene, 1-propanol, 2-propanol, 1-butanol and *t*-butanol at 303.15, 308.15, 313.15, 318.15 and 323.15 K. Some literature values are cited in the table, showing good agreement with our data. Viscosities of the systems, *m*-xylene + 1-propanol, *m*-xylene + 2-propanol, *m*-xylene + 1-butanol and *m*-xylene + *t*-butanol have been shown in table 2 at different temperatures. The data have been fitted to a polynomial equation of the form,

$$\eta \, (\mathrm{kg}\,\mathrm{m}^{-1}\,\mathrm{s}^{-1}) = \sum_{i=0}^{n} A_i x_2^i \tag{1}$$

where x_2 is the mole fraction of alkanols. The coefficients, A_i , of the equation and squares of regression coefficients, r^2 , are shown in table 3. Viscosities of the systems as a function of mole fraction of alkanols at 303.15 K are represented graphically in figure 1. The curves have been smoothed by the above equation. Since the basic nature of the viscosity curves of the systems virtually does not change with temperature, the curves for other temperatures are not shown.

Examination of the curves shows that addition of alkanols to m-xylene increases viscosity slowly up to a substantial concentration of alkanols, following which the viscosity increases rapidly with increasing concentration of alkanols. In the

		Temperature (K)										
Compound		303.15	308.15	313.15	318.15	323.15						
<i>m</i> -Xylene	ρ	0.8554 (0.8553) ^a	0.8511 (0.8521) ^a	0.8468	0.8425	0.8381						
	η	5.528 (5.47) ^b (5.55) ^c	5.248 (5.17) ^b (5.27) ^c	4.973	4.717	4.478						
1-Propanol	ρ	$\begin{array}{c} 0.7953 \\ (0.7956)^{d,e} \\ (0.7954)^{f} \\ (0.7955)^{g} \end{array}$	$\begin{array}{c} 0.7912 \\ (0.7912)^{\rm d} \\ (0.7913)^{\rm f} \end{array}$	$\begin{array}{c} 0.7871 \\ (0.7874)^{\rm e} \\ (0.7871)^{\rm f} \end{array}$	0.7830	0.7789 (0.7789) ^h						
	η	(17.309) $(17.21)^{d}$ $(17.25)^{i}$	${ \begin{array}{c} 15.440 \\ (15.26)^{d,f,j} \\ (15.46)^k \end{array} }$	$\begin{array}{c} 13.80 \\ (13.72)^{\rm f} \\ (13.66)^{\rm j} \\ (13.85)^{\rm k} \end{array}$	12.253 (12.45) ^j	11.02 (11.21) ^j						
2-Propanol	ρ	$0.7768 \\ (0.7769)^1 \\ 17.069$	0.7724 (0.7725) ^d	$\begin{array}{c} 0.7679 \\ (0.7683)^1 \end{array}$	$0.7634 \\ (0.7636)^{1}$	$\begin{array}{c} 0.7588 \\ (0.7589)^{l} \end{array}$						
	η	$(1.81)^{d}$	(0.7726) 15.504 $(15.51)^{d}$	13.474	11.784	10.307						
1-Butanol	ρ	(0.8019) $(0.8018)^{d,g}$ $(0.80194)^{m}$	(0.7980) $(0.7981)^{d,k}$	$\begin{array}{c} 0.7941 \\ (0.7943)^{\mathrm{k}} \\ (0.79405)^{\mathrm{m}} \end{array}$	0.7902	$0.7863 \\ (0.7862)^{h} \\ (0.7865)^{j}$						
	η	$\begin{array}{c} 22.924 \\ (22.62)^{\rm b} \\ (22.68)^{\rm d} \\ (22.46)^{\rm f} \end{array}$	$\begin{array}{c} 20.254 \\ (19.82)^{\rm d,f} \\ (20.17)^{\rm k} \end{array}$	$\begin{array}{c} 17.949 \\ (17.64)^{\rm f,j} \\ (17.93)^{\rm k} \end{array}$	15.937 (15.75) ^j	14.237 (14.06) ^j						
t-Butanol	ρ	$(0.7754)^{i}$	(0.7704) $(0.7643)^{d}$	0.7650	0.7599	0.7546						
	η	$\begin{array}{c} 33.401 \\ (33.59)^{\rm f} \\ (33.16)^{\rm i} \\ (33.653)^{\rm n} \end{array}$	26.122 (26.23) ^f	20.964 (20.807) ⁿ	17.003	14.144						

Table 1. Densities, $\rho \times 10^{-3}$ (kg m⁻³) and viscosities, $\eta \times 10^4$ (kg m⁻¹ s⁻¹) of pure compounds at different temperatures.

^aRef [10]; ^bRef [5]; ^cRef [3]; ^dRef [6]; ^cRef [12]; ^fRef [2]; ^gRef [14]; ^hRef [15]; ⁱRef [4]; ^jRef [8]; ^kRef [7]; ^lRef [11]; ^mRef [13]; ⁿRef [9].

solution systems of m-xylene + alkanols we envisage the presence of the following types of interactions:

- (i) Donor-acceptor interaction between π -electrons of aromatic ring and alkanols.
- (ii) In *m*-xylene-rich region disintegration of multimers of alkanols into smaller units.
- (iii) In alkanol-rich region, the smaller units of alkanols, formed in (ii), are believed to be reformed into larger units of multimers.

The slow rise of viscosity (figure 1) can be accounted for primarily due to dissociation of alkanols as expressed in (ii). In alkanol-rich region the rapid rise of viscosity is thought to be due to the factor mentioned in (iii) above.

Excess viscosity, η^{E} , has been calculated by using the following equation,

$$\eta^{\rm E} = \eta - \exp(x_1 \ln \eta_1 + x_2 \ln \eta_2) \tag{2}$$

where η_1 and η_2 are the viscosities of the components, *m*-xylene and alkanols respectively. η is the viscosity of the solution. x_1 and x_2 are the mole fractions

Table 2. Viscosities, $\eta \times 10^4$ (kg m⁻¹ s⁻¹), excess viscosities, $\eta^{\rm E} \times 10^4$ (kg m⁻¹ s⁻¹), of the systems, *m*-xylene, +1-propanol, +2-propanol, +1-butanol and +*t*-butanol at different temperatures.

$T(\mathbf{K})$	303.15		308.15		313	313.15		318.15		323.15	
x_2	η	$\eta^{\rm E}$	η	$\eta^{\rm E}$	η	$\eta^{\rm E}$	η	$\eta^{\rm E}$	η	$\eta^{\rm E}$	
m -Xylene $(x_1) + 1$ -propagol (x_2)											
0.0000	5.528	0.000	5.248	0.000	4.973	0.000	4.717	0.000	4.478	0.000	
0.1010	5.574	-0.626	5.251	-0.576	4.970	-0.529	4.710	-0.476	4.462	-0.440	
0.1999	5.809	-1.131	5.459	-1.028	5.138	-0.947	4.847	-0.854	4.578	-0.782	
0.2988	6.153	-1.617	5.763	-1.457	5.401	-1.333	5.076	-1.191	4.778	-1.080	
0.3969	6.660	-2.032	6.190	-1.841	5.774	-1.671	5.395	-1.488	5.047	-1.353	
0.4996	7.417	-2.357	6.834	-2.142	6.336	-1.934	5.883	-1.710	5.466	-1.554	
0.5988	8.377	-2.569	7.670	-2.325	7.048	-2.106	6.503	-1.846	5.995	-1.682	
0.6993	9.695	-2.583	8.819	-2.326	8.037	-2.108	7.361	-1.895	6.740	-1.664	
0.7931	11.369	-2.297	10.245	-2.094	9.283	-1.883	8.434	-1.620	7.679	-1.467	
0.8961	13.844	-1.529	12.412	-1.384	11.151	-1.256	10.055	-1.039	9.091	-0.943	
1.0000	17.309	0.000	15.440	0.000	13.800	0.000	12.253	0.000	11.020	0.000	
<i>m</i> -Xylei	ne $(x_1) + 2$	-propanol	(x_2)								
0.0000	5.528	0.000	5.248	0.000	4.973	0.000	4.717	0.000	4.478	0.000	
0.1078	5.524	-0.749	5.215	-0.683	4.936	-0.602	4.668	-0.539	4.419	-0.480	
0.1980	5.645	-1.328	5.316	-1.187	5.009	-1.049	4.736	-0.919	4.461	-0.820	
0.2991	5.885	-1.967	5.520	-1.736	5.175	-1.526	4.875	-1.328	4.576	-1.171	
0.3999	6.249	-2.588	5.852	-2.241	5.426	-1.982	5.099	-1.704	4.782	-1.467	
0.4994	6.771	-3.160	6.259	-2.756	5.787	-2.394	5.372	-2.079	4.980	-1.810	
0.6002	7.626	-3.552	6.979	-3.075	6.399	-2.647	5.887	-2.285	5.424	-1.962	
0.6992	8.765	-3.790	7.929	-3.264	7.172	-2.812	6.543	-2.404	5.964	-2.058	
0.8024	10.519	-3.652	9.407	-3.110	8.433	-2.632	7.606	-2.280	6.848	-1.899	
0.9010	13.369	-2.539	11.814	-2.114	10.444	-1.764	9.286	-1.534	8.269	-1.222	
1.0000	17.868	0.000	15.504	0.000	13.4/4	0.000	11./84	0.000	10.307	0.000	
<i>m</i> -Xyleı	$1 = (x_1) + 1$	-butanol (x	(c ₂)								
0.0000	5.528	0.000	5.248	0.000	4.973	0.000	4.717	0.000	4.478	0.000	
0.0994	5.716	-0.672	5.362	-0.648	5.083	-0.573	4.808	-0.528	4.561	-0.485	
0.2000	6.105	-1.263	5.719	-1.165	5.370	-1.065	5.060	-0.971	4.780	-0.886	
0.3000	6.618	-1.873	6.175	-1.703	5.779	-1.535	5.416	-1.393	5.099	-1.258	
0.4003	7.363	-2.426	6.837	-2.183	6.360	-1.959	5.918	-1.774	5.532	-1.604	
0.5001	8.416	-2.862	7.739	-2.581	7.125	-2.329	6.594	-2.089	6.130	-1.876	
0.6003	9.824	-3.178	8.957	-2.856	8.190	-2.561	7.499	-2.307	6.922	-2.063	
0.7002	11.780	-3.201	10.648	-2.869	9.635	-2.585	8.755	-2.317	8.002	-2.078	
0.8002	14.385	-2.880	12.869	-2.600	11.571	-2.321	10.431	-2.071	9.456	-1.854	
0.8998	17.949	-1.938	16.013	-1.680	14.225	-1.560	12.737	-1.3/3	11.454	-1.231	
1.0000	22.924	0.000	20.234	0.000	17.949	0.000	15.957	0.000	14.237	0.000	
<i>m</i> -Xylei	$te(x_1) + t - \frac{1}{5}$	butanol (x	²)	0.000	4.072	0.000	4 7 1 7	0.000	4 470	0.000	
0.0000	5.528	0.000	5.248	0.000	4.9/3	0.000	4./1/	0.000	4.4/8	0.000	
0.0997	5.637	-0.992	5.313	-0.848	5.014	-0./29	4./42	-0.628	4.489	-0.538	
0.1997	5.878	-2.056	5.527	-1.706	5.185	-1.447	4.881	-1.222	4.601	-1.037	
0.3000	6.247	-3.253	5.835	-2.661	5.453	-2.207	5.100	-1.839	4.789	-1.539	
0.3998	6.778	-4.587	6.291	-3.681	5.842	-3.001	5.432	-2.453	5.066	-2.030	
0.4999	/.520	-6.084	6.919	-4./90	6.375	-5.857	5.884	-3.0/9	5.453	-2.509	
0.399/	8.655	-/.620	/.860	-5.885	/.165	-4.624	0.546	-3.638	0.004	-2.925	
0.7002	10.329	-9.105	9.23/	-0.901	8.303	-5.519	/.4/5	-4.108	0.783	-5.239	
0.8000	15.569	-9.952	11.0/0	-/.281	10.216	-5.508	9.015	-4.14/	8.036	-5.204	
0.9004	19.191	-8./38	10.034	-0.231	13.600	-4.566	11.642	-3.326	10.103	-2.512	
1.0000	33.401	0.000	20.122	0.000	20.964	0.000	17.003	0.000	14.143	0.000	

Table 3. Coefficients, A_{i} , of equation (1), expressing viscosity, $\eta \times 10^4$ (kg m⁻¹ s⁻¹) and the squares of the regression coefficients, r^2 , for the systems, *m*-xylene, +1-propanol, +2-propanol, +1-butanol and +*t*-butanol.

System	$T(\mathbf{K})$	A_0	A_1	A_2	A_3	A_4	A_5	r^2
<i>m</i> -Xylene + 1-propanol	303.15 308.15 313.15 318.15 323.15	-0.4794 -1.2112 -1.1014 -0.8027 -0.9619	11.353 16.201 13.398 8.5841 9.5928	-15.572 -36.013 -27.320 -8.7218 -15.202	27.146 62.213 45.957 7.6423 19.053	-19.092 -48.606 -35.352 1.2569 -8.3512	8.4281 17.612 13.246 -0.4206 2.4123	0.9999 0.9999 >0.9999 0.9999 >0.9999
<i>m</i> -Xylene + 2-propanol	303.15 308.15 313.15 318.15 323.15	$\begin{array}{r} -0.6667 \\ -0.9598 \\ -0.589 \\ -1.0455 \\ -0.9551 \end{array}$	7.8683 7.2515 2.0818 6.721 3.5037	-14.585 -5.243 12.837 -6.1497 9.0341	42.502 8.4942 -26.377 3.56 -30.865	-53.223 -10.644 21.952 1.0028 35.517	$30.453 \\ 11.364 \\ -1.3971 \\ 2.983 \\ -10.402$	0.9999 0.9999 0.9999 0.9999 0.9999
<i>m</i> -Xylene + 1-butanol	303.15 308.15 313.15 318.15 323.15	$\begin{array}{r} 0.7536 \\ 0.0231 \\ -0.1879 \\ -0.1149 \\ -0.0112 \end{array}$	15.129 15.15 16.277 12.801 10.375	-38.028 -27.832 -40.639 -27.246 -20.485	87.214 47.991 79.615 50.034 37.991	-79.081 -32.724 -67.743 -39.246 -30.1800	31.412 12.404 25.655 14.991 12.070	>0.9999 0.9999 >0.9999 >0.9999 >0.9999
<i>m</i> -Xylene + <i>t</i> -butanol	303.15 308.15 313.15 318.15 323.15	-5.7323 -4.3192 -2.951 -1.873 -1.5177	99.95 72.11 48.054 29.955 22.558	-488.37 -338.31 -217.32 -128.75 -92.061	1142 777.14 499.15 297.17 209.31	-1231.1 -826.44 -532.4 -319.34 -222.43	511.1 340.67 221.45 135.12 93.804	>0.9999 >0.9999 >0.9999 >0.9999 >0.9999



Figure 1. Comparison of viscosities of the systems, *m*-xylene (x_1) + alkanols (x_2) , as a function of mole fraction of alkanols, x_2 , at 303.15 K.

System	<i>T</i> (K)	A_0	A_1	A_2	A_3	σ
<i>m</i> -Xylene + 1-propanol	303.15	-9.4587	-5.5739	-3.3702	-0.7687	0.01082
	308.15	-8.5571	-5.0541	-3.1271	-0.6484	0.01188
	313.15	-7.7487	-4.4849	-2.9207	0.5990	0.0082
	318.15	-6.8997	-4.0564	-2.1788	0.4839	0.02272
	323.15	-6.2404	-3.4624	-1.9756	0.1508	0.00606
<i>m</i> -Xylene + 2-propanol	303.15	-12.4790	-10.1351	-8.6051	-4.7346	0.02069
	308.15	-10.8623	-8.7251	-7.0715	-2.8925	0.03276
	313.15	-9.7473	-7.2478	-9.7765	-2.2057	0.09228
	318.15	-8.1729	-6.0756	-4.8114	-1.9081	0.02190
	323.15	-7.1011	-5.2542	-3.6925	-0.4989	0.02923
<i>m</i> -Xylene + 1-butanol	303.15	-11.4382	-7.7273	-4.4409	-1.6913	0.02122
	308.15	-10.3048	-7.0554	-4.0309	-0.4287	0.02352
	313.15	-9.2519	-6.1352	-3.8265	-1.0820	0.01480
	318.15	-8.3423	-5.4711	-3.3260	-0.6086	0.01057
	323.15	-7.4911	-4.7989	-3.0587	-0.5966	0.00881
<i>m</i> -Xylene + <i>t</i> -butanol	303.15	-23.4837	-28.7716	-42.7637	-37.6110	0.29149
	308.15	-18.6125	-21.0805	-28.9787	-24.4326	0.19677
	313.15	-14.9734	-15.7080	-20.4279	-16.4922	0.12576
	318.15	-12.0784	-11.6677	-14.1226	-10.7139	0.07741
	323.15	-9.8816	-8.8447	-10.1194	-7.3617	0.05402

Table 4. Coefficients, A_i , of Redlich–Kister equation (equation (2)), expressing, $\eta^{\rm E} \times 10^4$ (kg m⁻¹ s⁻¹) and standard deviations, σ , for the systems.

of *m*-xylene and alkanols. The excess values are shown in table 2. The values have been fitted to a Redlich-Kister polynomial equation of the type,

$$\eta^{\rm E} = x_1 x_2 \sum_{i=0}^{n} A_i (1 - 2x_1)^i.$$
(3)

The coefficients of the equation, A_i , and standard deviations, σ , are listed in table 4. The excess viscosities, $\eta^{\rm E}$, for different systems are plotted in figures 2–5 at 303.15, 308.15, 313.15, 318.15 and 323.15 K as a function of mole fraction of alkanols. The curves are smoothed by the above equation.

Examination of the curves shows that:

- (i) $\eta^{\rm E}$ are negative for the whole range of composition.
- (ii) The minima occur between 0.65 and 0.80 mole fraction of alkanols.
- (iii) With the rise of temperature the magnitude of negative $\eta^{\rm E}$ decreases, i.e., $\delta \eta^{\rm E} / \delta T$ is positive.

The negative excess viscosities throughout the whole range of composition indicate the formation of smaller units of alkanols in different proportions depending upon the concentration of alkanols in the solution systems.

Figure 6 shows the comparison of the variation of excess viscosities of different systems as a function of mole fraction of alkanols at 303.15 K. Examination of the curves reveals that the branched chain alkanols, 2-propanol and *t*-butanol, show larger negative η^{E} than their straight chain isomers, 1-propanol and 1-butanol, respectively. This leads us to conclude that branched chain alkanols reduce the viscosity more than their straight chain isomers do. Akhtar *et al.* [1] in a viscometric study of solutions of three isomers of pentanol in toluene observed that the magnitude of negative η^{E} follows the order, toluene + 3-pentanol > toluene +2-pentanol > toluene + 1-pentanol



Figure 2. Excess viscosity of the system, *m*-xylene (x_1) + 1-propanol (x_2) , at different temperatures.



Figure 3. Excess viscosity of the system, *m*-xylene (x_1) + 2-propanol (x_2) , at different temperatures.



Figure 4. Excess viscosity of the system, *m*-xylene $(x_1) + 1$ -butanol (x_2) , at different temperatures.



Figure 5. Excess viscosity of the system, *m*-xylene $(x_1) + t$ -butanol (x_2) , at different temperatures.



Figure 6. Comparison of excess viscosities of the systems, *m*-xylene (x_1) + alkanols (x_2) , against mole fraction of alkanols (x_2) at 303.15 K. \blacktriangle *m*-xylene + 1-propanol, \ast *m*-xylene + 2-propanol, \blacklozenge *m*-xylene + 1-butanol, \blacklozenge *m*-xylene + *t*-butanol.

in the temperature range 303.15 to 323.15 K, confirming our conclusion. Saleh *et al.* [16] also reported similar observation for solutions of 1-pentanol, 2-pentanol and 3-pentanol in *n*-heptane. In a study of the viscometric properties of different alkanols in toluene, Nikam *et al.* [2] showed the effects of branching and chain length of alkanols, which are consistent with our observation. We wish to put forward a plausible explanation on the effect of branched chain alkanols compared to straight chain alkanols on the viscosity of *m*-xylene + alkanol systems. Branched chain alkanols are less strongly associated than *n*-alkanols through H-bonding, because of steric hindrance, and hence more easily dissociable into smaller units. Moreover, the interaction between π -electrons of aromatic ring and branched chain alkanols is weaker than that between aromatic ring and *n*-alkanols, again due to steric effect. Thus, the branched chain alkanols cause greater reduction of viscosity from ideal values, i.e., larger negative $\eta^{\rm E}$, than their straight chain isomers do. In a recent study, Saleh *et al.* [17] used the same argument to explain the volumetric properties of the present systems.

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