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Viscosity of Some Binary Mixtures of Arenes

B. S. Lark,[1] M. Mehra,[1] S. L. Oswal,[2, 3] and N. Y. Ghael[2]

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The viscosity η of 12 binary mixtures of benzene + toluene, + ethylbenzene, + isopropylbenzene, + *tert*-butylbenzene; toluene + ethylbenzene, + isopropylbenzene, + *tert*-butylbenzene; ethylbenzene + isopropylbenzene; isopropylbenzene + *tert*-butylbenzene; *o*-xylene + *m*-xylene; *m*-xylene + *p*-xylene; and *p*-xylene + *o*-xylene has been measured over the entire range of composition. The viscosity deviations $\Delta\eta$ and excess Gibbs energy of activation ΔG^{*E} of viscous flow based on Eyring's theory have been calculated. The results have been analyzed in terms of the change in the structure of pure component molecules. The viscosity data have been correlated with the equations of Grunberg and Nissan; Hind, McLaughlin, and Ubbelohde; Tamura and Kurata; Katti and Chaudhri; McAllister; and Heric and Brewer. The Prigogine–Flory–Patterson–Bloomfield–Dewan (PFPBD) theory has been applied to analyze the excess viscosity of the present binary mixtures.

KEY WORDS: arenes; Gibbs energy of activation; liquid mixtures; molecular interactions; viscosity.

1. INTRODUCTION

We have been engaged in a systematic study of the thermodynamic, acoustic, and transport properties of binary liquid mixtures containing cycloalkane, alkane, and aromatic hydrocarbons [1–5]. In earlier papers [1, 2] speeds of sound, isentropic compressibilities, excess molar volumes, and excess isentropic compressibilities for aromatic hydrocarbon + aromatic hydrocarbon binary mixtures have been reported which interact only weakly. It has been shown that excess properties depend directly on systematic changes in the shape and size of the component molecules. In this

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[1] Department of Chemistry, Guru Nanak Dev University, Amritsar 143 005, India.

[2] Department of Chemistry, South Gujarat University, Surat 395 007, India.

[3] To whom correspondence should be addressed. E-mail: oswalsl@satyam.net.in

paper we extend our studies to the viscosity behavior of aromatic hydrocarbon + aromatic hydrocarbon binary mixtures which is strongly dependent on the size and shape of the component molecules. This study will also be useful to examine various empirical equations used to correlate viscosity data of binary mixtures in terms of pure component properties and to examine the Prigogine–Flory–Patterson–Bloomfield–Dewan (PFPBD) theory [6–9].

2. EXPERIMENTS

2.1. Method

The viscosity η was measured with a modified suspended-level Ubbelohde viscometer [10]. The viscometer was designed so as to reduce surface tension effects to negligible values [11]. The details of the experimental procedure have been described earlier [12]. The apparatus was submerged in a thermostatic bath at 298.15 and 303.15 K with a resolution of ±0.05 K and allowed to attain thermal equilibrium. The viscometer has been calibrated so as to determine the two constants C and B in the equation $\eta/\rho = \mathrm{C}t - \mathrm{B}/t$, obtained by measuring the flow time t with pure water, benzene, toluene, isopropylbenzene, *o*-xylene, and *p*-xylene [13–15]. The flow time of a definite volume of liquid through the capillary was measured with an accurate stopwatch with a precision of ±0.1 s. Four to five sets of readings for the flow times were taken for each pure liquid or liquid mixture, and the arithmetic mean was taken from the calculations. The densities ρ required to convert kinematic viscosities into dynamic viscosities η were calculated from dilatometrically measured excess molar volumes reported earlier [1]. The mixtures were prepared by mixing known masses of pure liquids in airtight narrow-mouth stoppered bottles. The possible error in the mole fractions is estimated to be $< 10^{-4}$. The error in the viscosity η is estimated to less than 0.002 mPa · s.

2.2. Source and Purity of Samples

Benzene, toluene, *o*-, *m*-, and *p*-xylenes (BDH, AR), ethylbenzene, isopropylbenzene, and tertbutylbenzene (Fluka, AG) were shaken well with concentrated sulphuric acid to remove thiophene, washed well with water, and then fractionally distilled over phosphorous pentaoxide [14]. The middle fractions were retained. The purity of the various solvents was checked by determining the densities and refractive indices of purified components at 298.15 K (Table I), which agreed well with literature values [14–30].

Table I. Physical Constants of Various Solvents

Temp (K)	Density (g · cm^{-3})		Refractive index		Viscosity (mPa · s)	
	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
C_6H_6						
298.15	0.87368	0.87360 [14, 16] 0.87365 [17] 0.87368 [18]	1.4981	1.49792 [17]	0.6025	0.6028 [14]
303.15	0.86845	0.86829 [14, 16] 0.86843 [19] 0.86861 [20]			0.5563	0.5621 [14]
$C_6H_5CH_3$						
298.15	0.86228	0.86219 [16] 0.8623 [22]	1.4942	1.49413 [14, 21]	0.5513	0.5525 [14] 0.5544 [15]
303.15	0.85769	0.85754 [14, 16] 0.85760 [22] 0.85778 [20]			0.5198	0.5226 [22] 0.5221 [23]
$C_6H_5CH_2CH_3$						
298.15	0.86260	0.86253 [14] 0.86249 [24]	1.4930	1.49320 [14] 1.49298 [25]	0.6373	0.6373 [14]
303.15	0.85826	0.85815 [14]			0.5956	0.5963 [14]
$C_6H_5CH(CH_3)_2$						
298.15	0.85749	0.85743 [16]	1.4892	1.4889 [25]		
303.15	0.85823	0.85315 [16]			0.6870	0.6955 [26]
$C_6H_5C(CH_3)_3$						
298.15	0.86244	0.86111 [14]	1.4905	1.49684 [14]		
303.15	0.85830	0.85830 [14]			1.0003	
o-$C_6H_4(CH_3)_2$						
298.15	0.87594	0.87594 [14, 16] 0.87620 [21]	1.5032	1.5029 [14] 1.5028	0.7551	0.756 [14]
303.15	0.87172	0.87174 [14, 16] 0.87175 [27]			0.7040	0.7136 [14] 0.6930 [28]
m-$C_6H_4(CH_3)_2$						
298.15	0.85994	0.8600 [16] 0.8602 [21]	1.4947	1.49464 [14] 1.49443 [25]	0.5877	0.5810 [14]
303.15	0.85564	0.85581 [16] 0.85580 [29]			0.5590	0.547 [27]
p-$C_6H_4(CH_3)_2$						
298.15	0.85670	0.85661 [16] 0.8568 [30]	1.4934	1.49325 [14] 1.49286 [25]	0.6060	0.605 [14] 0.6045 [22]
303.15	0.85830	0.85225 [16] 0.85227 [27]			0.5670	0.566 [14] 0.567 [27, 29]

3. RESULTS

The density and viscosity data of the binary mixtures are presented in Table II. For five binary mixtures, benzene + ethylbenzene, toluene + ethylbenzene, *o*-xylene + *m*-xylene, *m*-xylene + *p*-xylene; and *p*-xylene + *o*-xylene, measurements have been carried out at two temperatures, 298.15 and 303.15 K, while for the remaining seven mixtures only at 303.15 K. For a compact and smooth representation of the data, the values of η were fitted with a polynomial equation of the form,

$$\eta = \sum_{i=0}^{m} \mathrm{A}_{\mathrm{i}} x_1^i \tag{1}$$

where x_1 is the mole fraction of the first component. The coefficients A_{i}, obtained from a least-squares fit with equal weights assigned to each point, are listed in Table III together with the standard deviations σ.

The viscosity deviations from a linear dependence on mole fraction are calculated from

$$\Delta\eta = \eta - \sum_{i=1}^{2} x_i \eta_i \tag{2}$$

where η and η_i represent the viscosities of the mixture and of the pure component i, respectively. The excess viscosity $\Delta \ln \eta$ has been calculated as [31]

$$\Delta \ln \eta = \ln \eta - \left(\sum_{i=1}^{2} x_i \ln \eta_i \right) \tag{3}$$

The term in parentheses ( ) is considered as the logarithm of the viscosity of an ideal mixture.

On the basis of the theory of absolute reaction rates [32], the excess Gibbs energy of activation $\Delta G^{*\mathrm{E}}$ of viscous flow may be calculated from

$$\Delta G^{*\mathrm{E}} = \mathrm{R}T\{\ln(\eta V/\eta_2 V_2) - x_1 \ln(\eta_1 V_1/\eta_2 V_2)\} \tag{4}$$

where V is the molar volume of the mixture and V_i is the molar volume of the pure component i. $\Delta G^{*\mathrm{E}}$ results are included in Table II. The estimated uncertainty of $\Delta G^{*\mathrm{E}}$ is about 15 $\mathrm{J \cdot mol^{-1}}$. The values of $\Delta\eta$, $\Delta \ln \eta$, and

Table II. Densities, Viscosities, and Gibbs Energies of Activation of Viscous Flow of Binary Mixtures. (Here x_1 is the mole fraction of first component.)

x_1	ρ $(\mathrm{cm^3 \cdot mol^{-1}})$	η $(\mathrm{mPa \cdot s})$	ΔG^{*E} $(\mathrm{J \cdot mol^{-1}})$	x_1	ρ $(\mathrm{cm^3 \cdot mol^{-1}})$	η $(\mathrm{mPa \cdot s})$	ΔG^{*E} $(\mathrm{J \cdot mol^{-1}})$
$C_6H_6 + C_6H_5CH_3$ at 303.15 K							
0.0529	0.85804	0.5206	−2	0.5963	0.86293	0.5372	−7
0.1185	0.85850	0.5220	−4	0.7138	0.86436	0.5426	−3
0.2615	0.85961	0.5257	−7	0.8413	0.86608	0.5482	−3
0.3482	0.86037	0.5277	−10	0.9558	0.86777	0.5538	−1
0.4486	0.86133	0.5312	−10				
$C_6H_6 + C_6H_5CH_2CH_3$ at 298.15 K				$C_6H_6 + C_6H_5CH_2CH_3$ at 303.15 K			
0.0268	0.86277	0.6320	−13	0.1358	0.85884	0.5881	6
0.1358	0.86370	0.6249	−15	0.2562	0.85959	0.5827	14
0.2562	0.86479	0.6202	−8	0.3579	0.86036	0.5777	15
0.3579	0.86578	0.6177	0	0.4426	0.86109	0.5744	18
0.4426	0.86665	0.6157	6	0.5472	0.86209	0.5710	22
0.5472	0.86779	0.6134	12	0.6302	0.86297	0.5678	21
0.6302	0.86876	0.6115	15	0.7423	0.86432	0.5637	17
0.7423	0.87015	0.6080	11	0.8318	0.86556	0.5608	12
0.8318	0.87132	0.6056	8	0.9404	0.86732	0.5574	3
0.9404	0.87282	0.6027	0				
$C_6H_6 + C_6H_5CH(CH_3)_2$ at 303.15 K				$C_6H_6 + C_6H_5C(CH_3)_3$ at 303.15 K			
0.1245	0.85413	0.6683	22	0.0424	0.85840	0.9763	15
0.2644	0.85541	0.6483	42	0.1376	0.85872	0.9194	32
0.4246	0.85722	0.6265	56	0.2605	0.85930	0.8507	46
0.5391	0.85878	0.6111	57	0.4018	0.86023	0.7791	55
0.5606	0.85910	0.6069	51	0.5266	0.86128	0.725	66
0.6382	0.86033	0.5972	49	0.682	0.86297	0.6637	65
0.6478	0.86049	0.5958	48	0.7952	0.86454	0.6265	68
0.7409	0.86219	0.5819	30	0.865	0.86569	0.6036	59
0.831	0.86408	0.5721	21	0.9376	0.86707	0.5792	36
0.919	0.86620	0.5634	11				
$C_6H_5CH_3 + C_6H_5CH_2CH_3$ at 298.15 K				$C_6H_5CH_3 + C_6H_5CH_2CH_3$ at 303.15 K			
0.1427	0.86255	0.6196	−15	0.0366	0.86256	0.5902	−22
0.2444	0.86255	0.6090	−20	0.1427	0.86260	0.5808	−24
0.3777	0.86255	0.5992	−11	0.2444	0.86263	0.5729	−22
0.4928	0.86255	0.5905	−6	0.3777	0.86264	0.5639	−15
0.5425	0.86256	0.5867	−4	0.4928	0.86264	0.5556	−13
0.6355	0.86257	0.5789	−4	0.5425	0.86263	0.5522	−11
0.7353	0.86258	0.5716	−1	0.6355	0.86260	0.5450	−13
0.8573	0.86257	0.5614	−3	0.7353	0.86255	0.5371	−17
0.9453	0.86254	0.5549	−2	0.8573	0.86246	0.5280	−20
				0.9453	0.86238	0.5223	−18

Table II. *(Continued)*

x_1	ρ ($cm^3 \cdot mol^{-1}$)	η ($mPa \cdot s$)	ΔG^{*E} ($J \cdot mol^{-1}$)	x_1	ρ ($cm^3 \cdot mol^{-1}$)	η ($mPa \cdot s$)	ΔG^{*E} ($J \cdot mol^{-1}$)
$C_6H_5CH_3 + C_6H_5CH(CH_3)_2$ at 298.15 K				$C_6H_5CH_3 + C_6H_5C(CH_3)_3$ at 303.15 K			
0.1169	0.85371	0.6671	16	0.0457	0.85832	0.9740	15
0.2596	0.85431	0.6430	32	0.0865	0.85833	0.9490	22
0.3951	0.85489	0.6203	41	0.2449	0.85832	0.8605	54
0.508	0.85539	0.6016	45	0.3937	0.85826	0.7829	72
0.605	0.85583	0.5854	43	0.4453	0.85823	0.7568	74
0.7505	0.85651	0.5615	36	0.5167	0.8582	0.7206	69
0.8459	0.85696	0.5459	27	0.6672	0.85811	0.6507	57
0.9474	0.85744	0.5288	11	0.7678	0.85803	0.6057	35
				0.8687	0.85792	0.5626	4
				0.957	0.85778	0.5317	−5
				0.9788	0.85774	0.5253	−4
$C_6H_5CH_2CH_3 + C_6H_5C(CH_3)_3$ at 303.15 K				$C_6H_5CH(CH_3)_2 + C_6H_5C(CH_3)_3$ at 303.15			
0.0665	0.85353	0.6803	0	0.039	0.85811	0.9864	2
0.2184	0.85423	0.6652	0	0.1371	0.85764	0.9507	3
0.3499	0.85486	0.6527	1	0.2661	0.85703	0.9067	7
0.4904	0.85555	0.6394	0	0.4247	0.85625	0.8551	10
0.591	0.85606	0.6297	−1	0.4906	0.85592	0.8347	11
0.6984	0.85661	0.6197	−4	0.6105	0.85531	0.7984	13
0.8215	0.85727	0.6086	−6	0.7457	0.8546	0.7572	7
0.9361	0.8579	0.5996	−4	0.8708	0.85393	0.7224	5
				0.9592	0.85345	0.6981	2
o-$C_6H_4(CH_3)_2 + m$-$C_6H_4(CH_3)_2$ at 298.15 K				o-$C_6H_4(CH_3)_2 + m$-$C_6H_4(CH_3)_2$ at 303.15 K			
0.0817	0.86121	0.5998	0	0.0817	0.85694	0.5668	−12
0.1825	0.86282	0.6144	−3	0.1825	0.85854	0.5783	−19
0.2946	0.86462	0.6303	−9	0.2946	0.86033	0.5938	−17
0.4285	0.86676	0.6512	−11	0.4285	0.86247	0.6119	−19
0.5533	0.86877	0.6731	−7	0.5533	0.86448	0.631	−14
0.6715	0.87067	0.6924	−10	0.6715	0.86638	0.6486	−13
0.7904	0.87258	0.7148	−5	0.7904	0.86831	0.6675	−9
0.9000	0.87434	0.7349	−5	0.9001	0.87009	0.6859	−4
m-$C_6H_4(CH_3)_2 + p$-$C_6H_4(CH_3)_2$ at 298.15 K				m-$C_6H_4(CH_3)_2 + p$-$C_6H_4(CH_3)_2$ at 303.15 K			
0.0857	0.85695	0.6046	0	0.0856	0.85264	0.5666	1
0.1428	0.85713	0.6026	−3	0.1427	0.85284	0.5659	0
0.2528	0.85749	0.5998	−6	0.2528	0.85322	0.5651	1
0.3922	0.85795	0.5968	−8	0.3046	0.8534	0.5648	1
0.4740	0.85822	0.5955	−7	0.3922	0.85369	0.5643	2
0.5824	0.85857	0.5942	−4	0.474	0.85396	0.5641	5
0.6995	0.85894	0.5935	1	0.5823	0.85432	0.5636	7
0.8337	0.85937	0.5928	8	0.6995	0.85470	0.5627	7
0.9538	0.85975	0.5899	5	0.8339	0.85512	0.5614	7
				0.9538	0.85550	0.5602	6

Table II. *(Continued)*

x_1	ρ ($cm^3 \cdot mol^{-1}$)	η ($mPa \cdot s$)	ΔG^{*E} ($J \cdot mol^{-1}$)	x_1	ρ ($cm^3 \cdot mol^{-1}$)	η ($mPa \cdot s$)	ΔG^{*E} ($J \cdot mol^{-1}$)
o-$C_6H_4(CH_3)_2 + p$-$C_6H_4(CH_3)_2$ at 298.15 K				o-$C_6H_4(CH_3)_2 + p$-$C_6H_4(CH_3)_2$ at 303.15 K			
0.0748	0.85814	0.6114	−18	0.0902	0.85406	0.5764	−7
0.1866	0.86029	0.6242	−28	0.2065	0.85630	0.5904	−10
0.3032	0.86252	0.6410	−26	0.3178	0.85845	0.6040	−14
0.4147	0.86467	0.6549	−33	0.4339	0.8607	0.6204	−9
0.5702	0.86766	0.6779	−33	0.4577	0.86116	0.6237	−9
0.6823	0.86983	0.6995	−16	0.5832	0.86359	0.6420	−5
0.8109	0.87232	0.7176	−23	0.6243	0.86438	0.6474	−6
0.9402	0.87481	0.7417	−11	0.7864	0.86754	0.6729	2
				0.8933	0.86962	0.6889	3

ΔG^{*E} for each mixture have been fitted with the Redlich–Kister polynomial equation,

$$Y^E = x_1(1-x_1) \sum_{i=0}^{m} \mathrm{B}_i (1-2x_1)^i \tag{5}$$

The coefficients B_i of Eq. (5) and the standard deviations σ are given in Table IV.

Table III. Coefficients A_i and Standard Deviations $\sigma(\eta)$ of Eq. (1) for Viscosity η ($mPa \cdot s$) of Binary Mixtures

Mixture	T (K)	A_0	A_1	A_2	A_3	$\sigma(\eta)$
$C_6H_6 + C_6H_5CH_3$	303.15	0.5196	0.0180	0.0188		0.0003
$C_6H_6 + C_6H_5CH_2CH_3$	298.15	0.6353	−0.0773	0.0922	−0.0489	0.0010
	303.15	0.5953	−0.0528	0.0137		0.0003
$C_6H_6 + C_6H_5CH(CH_3)_2$	303.15	0.6863	−0.1348	−0.0329	0.0371	0.0010
$C_6H_6 + C_6H_5C(CH_3)_3$	303.15	1.0025	−0.6568	0.2925	−0.0797	0.0020
$C_6H_5CH_3 + C_6H_5CH_2CH_3$	298.15	0.6367	−0.1266	0.0852	−0.0449	0.0009
	303.15	0.5943	−0.0911	0.0298	−0.0143	0.0010
$C_6H_5CH_3 + C_6H_5CH(CH_3)_2$	303.15	0.6868	−0.1689	0.0022		0.0002
$C_6H_5CH_3 + C_6H_5C(CH_3)_3$	303.15	0.9996	−0.5753	0.0392	0.0544	0.0014
$C_6H_5CH_2CH_3 + C_6H_5CH(CH_3)_2$	303.15	0.6873	−0.1043	0.0117		0.0006
$C_6H_5CH(CH_3)_2 + C_6H_5C(CH_3)_3$	303.15	1.0003	−0.3681	0.0669	−0.0122	0.0004
o-$C_6H_4(CH_3)_2 + m$-$C_6H_4(CH_3)_2$	298.15	0.5882	0.1342	0.0324		0.0006
	303.15	0.5579	0.1124	0.0331		0.0007
m-$C_6H_4(CH_3)_2 + p$-$C_6H_4(CH_3)_2$	298.15	0.6068	−0.0392	0.0471	−0.0262	0.0008
	303.15	0.5667	−0.0042	−0.0029		0.0004
o-$C_6H_4(CH_3)_2 + p$-$C_6H_4(CH_3)_2$	298.15	0.6046	0.1031	0.0466		0.0016
	303.15	0.5671	0.0973	0.0720	−0.0321	0.0004

Table IV. Coefficient B_i and Standard Deviations σ of Eq. (5)

Mixture	Property	T (K)	B_0	B_1	B_2	σ
$C_6H_6 + C_6H_5CH_3$	$\Delta\eta(\mathrm{mPa\cdot s})$	303.15	−0.0194	−0.0014		0.0003
	$\Delta \ln \eta$		−0.0149	−0.0050		0.0006
	$\Delta G^{*E}\ (\mathrm{J\cdot mol^{-1}})$		−38.6	−12.8		1.6
$C_6H_6 + C_6H_5CH_2CH_3$	$\Delta\eta\ (\mathrm{mPa\cdot s})$	298.15	−0.0133	−0.0472	−0.0917	0.0023
	$\Delta \ln \eta$		0.0303	−0.0780	−0.1421	0.0035
	$\Delta G^{*E}\ (\mathrm{J\cdot mol^{-1}})$		75.9	−193.5	−357.1	8.8
	$\Delta\eta\ (\mathrm{mPa\cdot s})$	303.15	−0.0157	0.0004		0.0005
	$\Delta \ln \eta$		0.0304	−0.0043		0.0008
	$\Delta G^{*E}\ (\mathrm{J\cdot mol^{-1}})$		77.5	13.6		1.5
$C_6H_6 + C_6H_5CH(CH_3)_2$	$\Delta\eta\ (\mathrm{mPa\cdot s})$	303.15	−0.0279	0.0182		0.0012
	$\Delta \ln \eta$		0.0879	0.0141	−0.0293	0.0012
	$\Delta G^{*E}\ (\mathrm{J\cdot mol^{-1}})$		222.5	35.5	−83.2	2.9
$C_6H_6 + C_6H_5C(CH_3)_3$	$\Delta\eta\ (\mathrm{mPa\cdot s})$	303.15	−0.1762	−0.0335	0.0842	0.0010
	$\Delta \ln \eta$		0.0927	−0.0597	0.1277	0.0016
	$\Delta G^{*E}\ (\mathrm{J\cdot mol^{-1}})$		233.5	−150.4	319.2	3.9
$C_6H_5CH_3 + C_6H_5CH_2CH_3$	$\Delta\eta\ (\mathrm{mPa\cdot s})$	298.15	−0.0181	−0.0204	0.0270	0.0004
	$\Delta \ln \eta$		−0.0100	−0.0300	−0.0478	0.0007
	$\Delta G^{*E}\ (\mathrm{J\cdot mol^{-1}})$		233.5	−150.4	319.2	3.9
	$\Delta\eta\ (\mathrm{mPa\cdot s})$	303.15	−0.0077	−0.0146	−0.0492	0.0008
	$\Delta \ln \eta$		−0.0045	−0.0293	−0.203	0.0039
	$\Delta G^{*E}\ (\mathrm{J\cdot mol^{-1}})$		−11.4	−71.7	−509.2	9.7
$C_6H_5CH_3 + C_6H_5CH(CH_3)_2$	$\Delta\eta\ (\mathrm{mPa\cdot s})$	303.15	−0.0013	−0.0045		0.0002
	$\Delta \ln h$		0.0729	−0.0141		0.0004
	$\Delta G^{*E}\ (\mathrm{J\cdot mol^{-1}})$		183.7	−35.7		1.1
$C_6H_5CH_3 + C_6H_5C(CH_3)_3$	$\Delta\eta\ (\mathrm{mPa\cdot s})$	303.15	−0.1197	0.0498	−0.0516	0.0018
	$\Delta \ln \eta$		0.1222	0.0855	−0.1070	0.0036
	$\Delta G^{*E}\ (\mathrm{J\cdot mol^{-1}})$		307.8	211.6	−269.0	8.7
$C_6H_5CH_2CH_3 + C_6H_5CH(CH_3)_2$	$\Delta\eta\ (\mathrm{mPa\cdot s})$	303.15	−0.0151	0.0107		0.0006
	$\Delta \ln \eta$		−0.0056	0.0179		0.0011
	$\Delta G^{*E}\ (\mathrm{J\cdot mol^{-1}})$		−15.3	45.5		3.0
$C_6H_5CH(CH_3)_2 + C_6H_5C(CH_3)_3$	$\Delta\eta\ (\mathrm{mPa\cdot s})$	303.15	−0.0483	−0.0034		0.0005
	$\Delta \ln \eta$		0.0185	−0.0024		0.0006
	$\Delta G^{*E}\ (\mathrm{J\cdot mol^{-1}})$		44.3	−6.5		1.4
$o\text{-}C_6H_4(CH_3)_2 + m\text{-}C_6H_4(CH_3)_2$	$\Delta\eta\ (\mathrm{mPa\cdot s})$	298.15	−0.0311	0.0075		0.0007
	$\Delta \ln \eta$		−0.0149	0.0086		0.0011
	$\Delta G^{*E}\ (\mathrm{J\cdot mol^{-1}})$		−36.3	22.6		2.9
	$\Delta\eta\ (\mathrm{mPa\cdot s})$	303.15	−0.0370	−0.0127		0.0008
	$\Delta \ln \eta$		−0.0334	−0.0256		0.0014
	$\Delta G^{*E}\ (\mathrm{J\cdot mol^{-1}})$		−83.0	−65.3		3.2
$m\text{-}C_6H_4(CH_3)_2 + p\text{-}C_6H_4(CH_3)_2$	$\Delta\eta\ (\mathrm{mPa\cdot s})$	298.15	−0.0079	−0.0152	0.0304	0.0003
	$\Delta \ln \eta$		−0.0127	−0.0258	0.0511	0.0005
	$\Delta G^{*E}\ (\mathrm{J\cdot mol^{-1}})$		−30.6	−63.8	127.4	1.2
	$\Delta\eta\ (\mathrm{mPa\cdot s})$	303.15	0.0053	−0.0076		0.0004
	$\Delta \ln \eta$		0.0055	−0.0217	0.0298	0.0009
	$\Delta G^{*E}\ (\mathrm{J\cdot mol^{-1}})$		13.1	−57.9	79.4	2.6

Table IV. *(Continued)*

Mixture	Property	T (K)	B_0	B_1	B_2	σ
o-$C_6H_4(CH_3)_2+p$-$C_6H_4(CH_3)_2$	$\Delta\eta$ (mPa·s)	298.15	−0.0445	−0.0039	−0.0475	0.0017
	$\Delta \ln \eta$		−0.0426	−0.0152	−0.0700	0.0025
	ΔG^{*E} (J·mol^{-1})		−103.6	−38.0	−177.5	6.4
	$\Delta\eta$ (mPa·s)	303.15	−0.0221	−0.0181		0.0004
	$\Delta \ln \eta$		−0.0125	−0.0305		0.0006
	ΔG^{*E} (J·mol^{-1})		−30.6	−80.6		1.6

4. CORRELATING EQUATIONS

Apart from expressing η as a polynomial fit, several semi-empirical relations have been proposed to estimate the dynamic viscosity η of liquid mixtures in terms of pure-component data [26, 33]. We have examined equations proposed by Grunberg and Nissan [34], Tamura and Kurata [35], Hind, McLaughlin, and Ubbelohde [36], Katti and Chaudhri [37], McAllister [38], and Heric and Brewer [39].

The Grunberg–Nissan phenomenological equation [34] is expressed as

$$\eta = \exp(x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12}) \tag{6}$$

where G_{12} is a parameter proportional to the interchange energy and has been regarded as an indicator for the nonideal behavior of binary mixtures. The semi-empirical equation due to Tamura and Kurata [35] is

$$\eta = x_1\phi_1\eta_1 + x_2\phi_2\eta_2 + 2(x_1x_2\phi_1\phi_2)^{1/2}\,C \tag{7}$$

where C is an adjustable parameter.

Hind, McLaughlin, and Ubbelohde [36] have proposed the following equation:

$$\eta = x_1^2\eta_1 + x_2^2\eta_2 + 2x_1x_2\eta_{12} \tag{8}$$

where η_{12} is attributed to unlike pair interactions. It is approximately equal to $0.5(\eta_1+\eta_2)$, but this relation is not sufficiently accurate for prediction purposes. This equation has been theoretically derived by Bearman and Jones [40] from statistical mechanical theory.

Katti and Chaudhri [37] derived the following equation:

$$\ln \eta V = x_1 \ln V_1\eta_1 + x_2 \ln V_2\eta_2 + x_1x_2W_{\text{vis}}/(\text{R}T) \tag{9}$$

where W_{vis} is an interaction term. All four above equations contain one adjustable parameter. The two-parameter McAllister equation [38] based on Eyring's theory of absolute reaction rates [32] and the three-body interaction model is

$$\begin{aligned}\ln \nu = {} & x_1^3 \ln \nu_1 + 3x_1^2x_2 \ln Z_{12} + 3x_1x_2^2 \ln Z_{21} + x_2^3 \ln \nu_2 - \ln(x_1 + x_2\text{M}_2/\text{M}_1) \\ & + 3x_1^2x_2 \ln(2/3 + \text{M}_2/3\text{M}_1) + 3x_1x_2^2 \ln(1/3 + 2\text{M}_2/3\text{M}_1) \\ & + x_2^3 \ln(\text{M}_2/\text{M}_1)\end{aligned} \tag{10}$$

where Z_{12} and Z_{21} are interaction parameters and M_i and ν_i are the molecular mass and kinematic viscosity of pure component i. The two-parameter Heric and Brewer equation [39] is of the form,

Table V. Values of the Parameters in Eqs. (6) to (9) and Standard Percentage Deviations $\sigma(\%)$ in Correlating the Viscosity of Binary Mixtures

	Eq. (6)		Eq. (7)		Eq. (8)		Eq. (9)	
Mixture	G_{12}	$\sigma(\%)$	C	$\sigma(\%)$	η_{12}	$\sigma(\%)$	$\text{W}_{\text{vis}}/\text{R}T$	$\sigma(\%)$
$C_6H_6 + C_6H_5CH_3$ [a]	−0.03	0.07	0.53	0.08	0.53	0.06	−0.02	0.08
$C_6H_6 + C_6H_5CH_2CH_3$ [b]	−0.07	0.66	0.60	0.81	0.60	0.69	−0.02	0.68
$C_6H_6 + C_6H_5CH_2CH_3$ [a]	−0.03	0.07	0.57	0.09	0.57	0.08	0.03	0.09
$C_6H_6 + C_6H_5CH(CH)_2$ [a]	−0.03	0.31	0.61	0.22	0.61	0.29	0.08	0.22
$C_6H_6 + C_6H_5C(CH_3)_3$ [a]	−0.02	0.63	0.67	1.00	0.71	0.67	0.14	0.77
$C_6H_5CH_3 + C_6H_5CH_2CH_3$ [b]	−0.03	0.30	0.58	0.33	0.58	0.31	−0.02	0.30
$C_6H_5CH_3 + C_6H_5CH_2CH_3$ [a]	−0.03	0.41	0.54	0.44	0.55	0.42	−0.07	0.87
$C_6H_5CH_3 + C_6H_5CH(CH_3)_2$ [a]	0.04	0.09	0.60	0.06	0.60	0.06	0.07	0.11
$C_6H_5CH_3 + C_6H_5C(CH_3)_3$ [a]	0.00	0.82	0.66	0.39	0.69	0.57	0.07	0.78
$C_6H_5CH_2CH_3 + C_6H_5CH(CH_3)_2$ [a]	−0.01	0.15	0.63	0.13	0.63	0.14	−0.01	0.15
$C_6H_5CH(CH_3)_2 + C_6H_5C(CH_3)_3$ [a]	0.01	0.06	0.81	0.08	0.82	0.07	0.02	0.06
$o\text{-}C_6H_4(CH_3)_2 + m\text{-}C_6H_4(CH_3)_2$ [b]	−0.01	0.09	0.66	0.10	0.66	0.10	−0.01	0.09
$o\text{-}C_6H_4(CH_3)_2 + m\text{-}C_6H_4(CH_3)_2$ [a]	−0.03	0.21	0.61	0.18	0.61	0.18	−0.03	0.21
$m\text{-}C_6H_4(CH_3)_2 + p\text{-}C_6H_4(CH_3)_2$ [b]	0.00	0.28	0.60	0.28	0.60	0.28	0.00	0.29
$m\text{-}C_6H_4(CH_3)_2 + p\text{-}C_6H_4(CH_3)_2$ [a]	0.01	0.10	0.57	0.10	0.57	0.10	0.01	0.16
$o\text{-}C_6H_4(CH_3)_2 + p\text{-}C_6H_4(CH_3)_2$ [b]	−0.07	0.36	0.65	0.35	0.65	0.34	−0.07	0.36
$o\text{-}C_6H_4(CH_3)_2 + p\text{-}C_6H_4(CH_3)_2$ [a]	−0.01	0.21	0.63	0.20	0.62	0.20	−0.01	0.21
Average $\langle\sigma(\%)\rangle$		0.28		0.29		0.27		0.32

[a] at 303.15 K.

[b] at 298.15 K.

$$\ln \nu = x_1 \ln \nu_1 + x_2 \ln \nu_2 + x_1 \ln \mathrm{M}_1 + x_2 \ln \mathrm{M}_2 + \ln(x_1 \mathrm{M}_1 + x_2 \mathrm{M}_2) + x_1 x_2 [\alpha_{12} + \alpha_{21}(x_1 - x_2)] \tag{11}$$

where α_{12} and α_{21} are adjustable parameters. The correlating ability of each of Eqs. (6) to (11), was tested by calculating the standard percentage deviations $\sigma(\%)$ between the experimental and the calculated viscosity as

$$\sigma\% = \left[\frac{1}{n-k} \sum \left\{ \frac{100(\eta_{\mathrm{exp}} - \eta_{\mathrm{cal}})}{\eta_{\mathrm{exp}}} \right\}^2 \right]^{1/2} \tag{12}$$

where n represents the number of data points and k is the number of numerical coefficients in the respective equation.

The results of the correlating equations, Eqs. (6) to (11), are compiled in Tables V and VI. The values of the different parameters and the percentage standard deviations $\sigma(\%)$ listed in Tables V and VI were obtained from the experimental viscosity data using the method of least squares.

Table VI. Values of the Parameters in Eqs. (9) to (11) and Standard Percentage Deviations $\sigma(\%)$ in Correlating Viscosities of Binary Mixtures

		Eq. (9)			Eq. (10)		
Mixture	Temp (K)	Z_{12}	Z_{21}	$\sigma(\%)$	α_{12}	α_{21}	$\sigma(\%)$
$C_6H_6 + C_6H_5CH_3$	303.15	0.62	0.61	0.05	−0.01	0.01	0.05
$C_6H_6 + C_6H_5CH_2CH_3$	298.15	0.71	0.69	0.65	−0.02	0.09	0.65
$C_6H_6 + C_6H_5CH_2CH_3$	303.15	0.66	0.67	0.08	0.03	0.00	0.08
$C_6H_6 + C_6H_5CH(CH)_2$	303.15	0.69	0.76	0.19	0.08	−0.02	0.19
$C_6H_6 + C_6H_5C(CH_3)_3$	303.15	0.81	0.95	0.66	0.14	0.06	0.66
$C_6H_5CH_3 + C_6H_5CH_2CH_3$	298.15	0.67	0.69	0.24	−0.02	0.02	0.24
$C_6H_5CH_3 + C_6H_5CH_2CH_3$	303.15	0.63	0.64	0.92	−0.07	0.04	0.92
$C_6H_5CH_3 + C_6H_5CH(CH_3)_2$	303.15	0.68	0.74	0.04	0.07	0.01	0.04
$C_6H_5CH_3 + C_6H_5C(CH_3)_3$	303.15	0.74	0.98	0.68	0.08	−0.10	0.68
$C_6H_5CH_2CH_3 + C_6H_5CH(CH_3)_2$	303.15	0.72	0.77	0.11	−0.01	−0.02	0.11
$C_6H_5CH(CH_3)_2 + C_6H_5C(CH_3)_3$	303.15	0.92	1.03	0.06	0.02	0.00	0.06
$o\text{-}C_6H_4(CH_3)_2 + m\text{-}C_6H_4(CH_3)_2$	298.15	0.79	0.74	0.11	−0.01	−0.01	0.11
$o\text{-}C_6H_4(CH_3)_2 + m\text{-}C_6H_4(CH_3)_2$	303.15	0.75	0.69	0.14	−0.03	0.03	0.14
$m\text{-}C_6H_4(CH_3)_2 + p\text{-}C_6H_4(CH_3)_2$	298.15	0.70	0.69	0.26	0.00	0.03	0.26
$m\text{-}C_6H_4(CH_3)_2 + p\text{-}C_6H_4(CH_3)_2$	303.15	0.67	0.66	0.13	0.01	0.02	0.13
$o\text{-}C_6H_4(CH_3)_2 + p\text{-}C_6H_4(CH_3)_2$	298.15	0.79	0.74	0.37	−0.07	0.01	0.37
$o\text{-}C_6H_4(CH_3)_2 + p\text{-}C_6H_4(CH_3)_2$	303.15	0.76	0.70	0.06	−0.01	0.03	0.06
Average $\langle\sigma(\%)\rangle$				0.279			0.279

5. DISCUSSION

The values of $\sigma(\%)$ are in the range from 0.07 to 1.00% for the single-parameter Eqs. (6) to (9), and from 0.04 to 0.92% for the two-parameter Eqs. (10) and (11). The average percentage standard deviations $\langle\sigma(\%)\rangle$ for Eqs. (6) to (9) with a single parameter are 0.28, 0.29, 0.27, and 0.32, respectively; and for Eqs. (10) and (11) with two parameters $\langle\sigma(\%)\rangle$ is 0.28. From an analysis of the present results it can be said that the use of the two-parameter Eqs. (10) and (11) for the present binary mixtures does not show any improvement over the correlating ability shown by single-parameter equations. All of the equations correlate binary viscosity data of aromatic hydrocarbon mixtures very well.

Figures 1 and 2 show that values of $\Delta\eta$ and ΔG^{*E} for $C_6H_6 + C_6H_5CH_3$, $+C_6H_5CH_2CH_3$, $+C_6H_5CH(CH_3)_2$, and $+C_6H_5C(CH_3)_3$ are small but negative over the entire range of composition. The values of $\Delta\eta$ at equimolar composition vary in the range from -0.003 to -0.044 mPa·s, and the values of ΔG^{*E} vary from -9 to 58 J·mol^{-1}. The magnitude of $\Delta\eta$ and ΔG^{*E} values for binary mixtures with the common component of benzene increases in the order $C_6H_5CH_3 < C_6H_5CH_2CH_3 < C_6H_5CH(CH_3)_2$

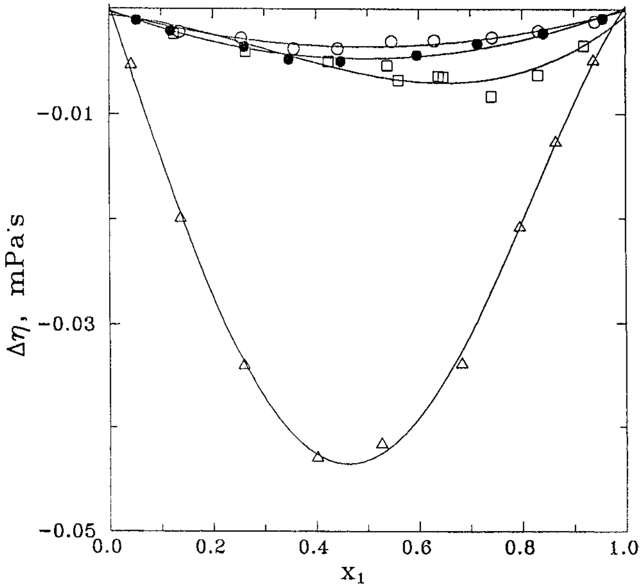

Fig. 1. Deviations of viscosity $\Delta\eta$ from linear additivity with mole fraction of benzene + alkyl benzene mixtures at 303.15 K. Experimental points: $C_6H_6 + C_6H_5CH_3$ (●), $+C_6H_5CH_2CH_3$ (○), $+C_6H_5CH(CH_3)_2$ (□), and $+C_6H_5C(CH_3)_3$ (△).

$< C_6H_5C(CH_3)_3$. Such behavior supports the earlier finding on the basis of H^E, K_S^E, V^E, and C_p^E [1, 2, 41–45] that the magnitude of deviations increases with an increase in size and complexity of substituted alkyl group in the benzene ring. This is clear from maximum deviations in viscosity observed for the case of $C_6H_6 + C_6H_5C(CH_3)_3$. It appears from comparing the results for benzene+alkylbenzene with the corresponding mixture of cyclohexane+alkylbenzene [46] that the dispersive forces present for mixtures involving cyclohexane are insignificant in benzene+alkylbenzene mixtures. The deviations from ideal solution behavior are only due to the structural changes in alkylbenzene molecules. For $C_6H_6 + C_6H_5CH_2CH_3$ the magnitude of viscosity deviations decreases with an increase in temperature from 298.15 to 303.15 K.

Figures 3 and 4 show that values of $\Delta\eta$ and ΔG^{*E} for $C_6H_5CH_3 + C_6H_5CH_2CH_3$, $+C_6H_5CH(CH_3)_2$, and $+C_6H_5C(CH_3)_3$; $C_6H_5CH_2CH_3 + C_6H_5CH(CH_3)_2$, and $C_6H_5CH(CH_3)_2 + C_6H_5C(CH_3)_3$ are negative but the magnitude is very small except for the mixtures involving $C_6H_5C(CH_3)_3$

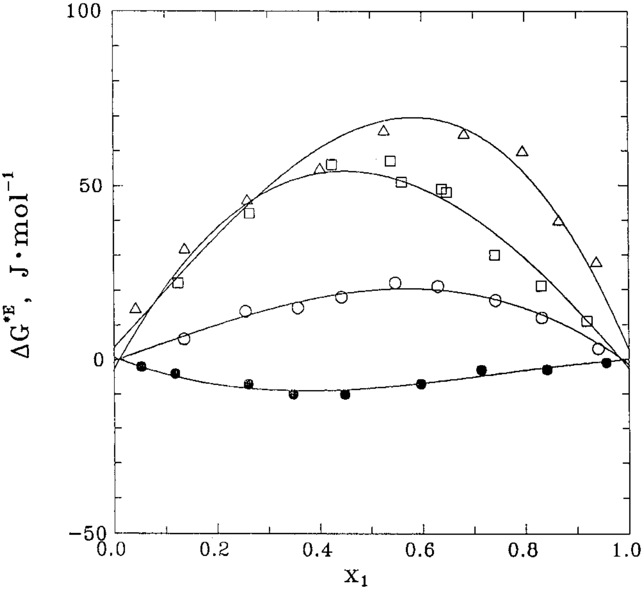

Fig. 2. Excess Gibbs energy of activation ΔG^{*E} of viscous flow for benzene+alkyl benzene mixtures at 303.15 K. Symbols same as in Fig. 1.

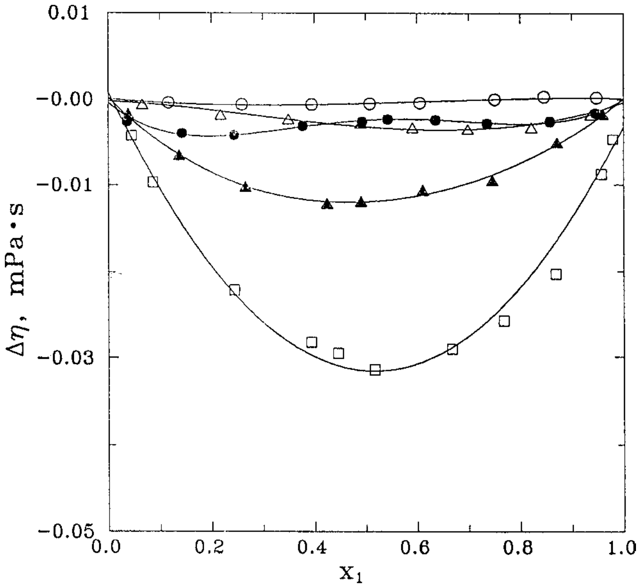

Fig. 3. Deviations of viscosity $\Delta\eta$ from linear additivity with mole fraction of alkyl benzene+aromatic hydrocarbon mixtures at 303.15 K. Experimental points: $C_6H_5CH_3+C_6H_5CH_2CH_3$ (●), $+C_6H_5CH(CH_3)_2$ (○), and $+C_6H_5C(CH_3)_3$ (□); $C_6H_5CH_2CH_3+C_6H_5CH(CH_3)_2$ (△) and $C_6H_5CH(CH_3)_2+C_6H_5C(CH_3)_3$ (▲).

molecules. Thus, the complexity in size and shape of $C_6H_5C(CH_3)_3$ molecules results in negative deviations in viscosity for alkylbenzene+alkylbenzene mixtures as was observed for benzene+alkylbenzene mixtures. With the substitution of an alkyl group in the benzene ring, a part of the mobile electron gets localized and, hence, the strength of the π-π interaction in substituted benzene is reduced. This explains the lower magnitudes of $\Delta\eta$ and ΔG^{*E} for the alkyl-substituted benzenes. For the $C_6H_6+C_6H_5CH_2CH_3$ mixture, the magnitude of $\Delta\eta$ is reduced by raising the temperature from 298.15 to 303.15 K.

The viscosity of three xylene mixtures, o-$C_6H_4(CH_3)_2+m$-$C_6H_4(CH_3)_2$, m-$C_6H_4(CH_3)_2+p$-$C_6H_4(CH_3)_2$, and o-$C_6H_4(CH_3)_2+p$-$C_6H_4(CH_3)_2$ have been reported at 298.15 and 303.15 K. The values of $\Delta\eta$ and ΔG^{*E} (Figs. 5 and 6) are small and negative. A similar trend was observed for the values of H^E and V^E [1, 47], which suggest that xylene mixtures are nearly ideal. The small deviations from ideality may be ascribed to the different position of methyl groups in xylene isomers.

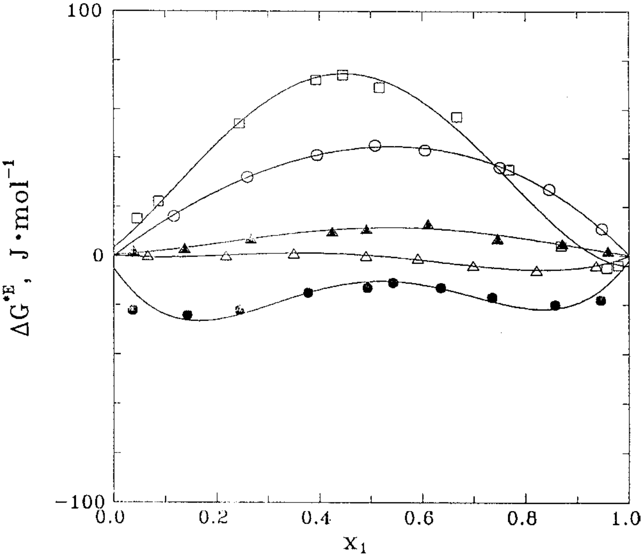

Fig. 4. Excess Gibbs energy of activation ΔG^{*E} of viscous flow for alkyl benzene + alkyl benzene mixtures at 303.15 K. Symbols same in Fig. 3.

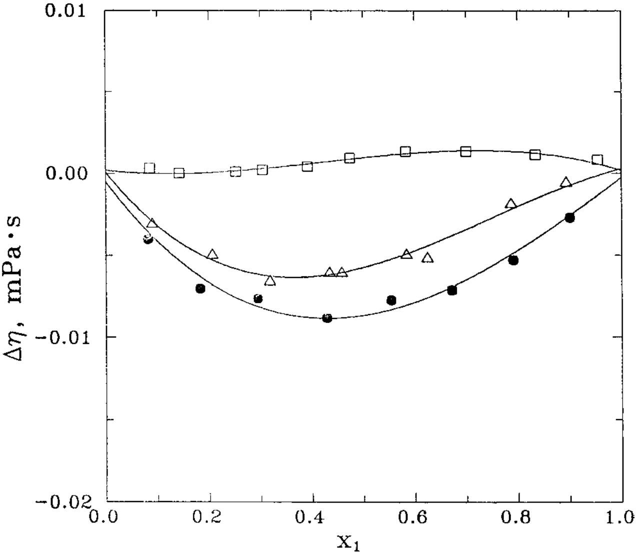

Fig. 5. Deviations of viscosity $\Delta\eta$ from linear additivity with mole fraction for xylene mixtures at 303.15 K. Experimental points: o-$C_6H_4(CH_3)_2$ + m-$C_6H_4(CH_3)_2$ (●), m-$C_6H_4(CH_3)_2$ + p-$C_6H_4(CH_3)_2$ (□), and o-$C_6H_4(CH_3)_2$ + p-$C_6H_4(CH_3)_2$ (△).

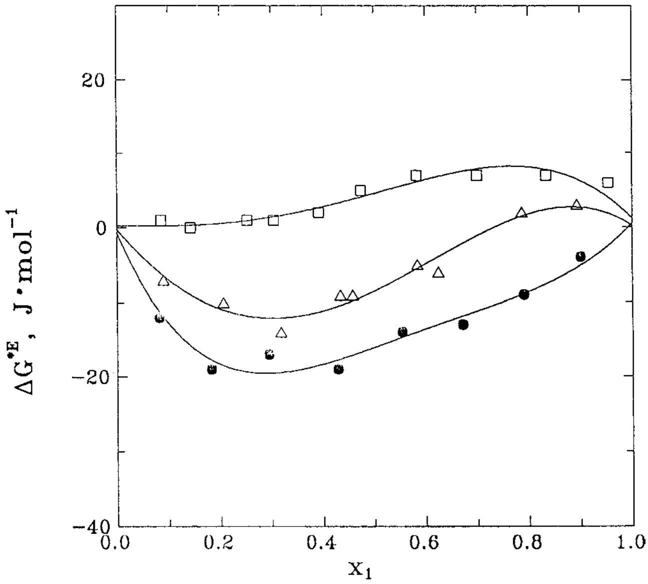

Fig. 6. Excess Gibbs energy of activation ΔG^{*E} of viscous flow for xylene mixtures at 303.15 K. Symbols same as in Fig. 5.

6. PRIGOGINE–FLORY–PATTERSON–BLOOMFIELD–DEWAN (PFPBD) THEORY

The PFPBD theory of non-electrolyte liquid mixtures [6–9] has been used to analyze the excess viscosity $\Delta \ln \eta$ for the present binary mixtures. The theoretical excess viscosity $\Delta \ln \eta_{\text{th}}$ is given by

$$\Delta \ln \eta_{\text{th}} = -\frac{H^{\text{E}}}{RT} + \frac{S^{\text{E}}}{R} + \frac{1}{\tilde{v}-1} - \left(\frac{x_1}{\tilde{v}_1 - 1} + \frac{x_2}{\tilde{v}_2 - 1}\right) \tag{13}$$

which can be written as

$$\Delta \ln \eta_{\text{th}} = \ln \eta(H) + \ln \eta(S) + \ln \eta(fv) \tag{14}$$

where

$$\ln \eta(H) = -H^{\text{E}}/(\text{R}T) \tag{15}$$

$$\ln \eta(S) = S^{\text{E}}/R \tag{16}$$

$$\ln \eta(fv) = \frac{1}{\tilde{v}-1} - \left(\frac{x_1}{\tilde{v}_1 - 1} + \frac{x_2}{\tilde{v}_2 - 1}\right) \tag{17}$$

The terms $\ln \eta(H)$, $\ln \eta(S)$, and $\ln \eta(fv)$ are the enthalpy, entropy, and free volume contributions, respectively, to $\Delta \ln \eta_{\text{th}}$. A positive value of the excess enthalpy H^{E} which entails a loss of cohesive energy upon mixing the pure liquids will give a negative contribution to $\Delta \ln \eta_{\text{th}}$ corresponding to a solution less viscous than the ideal solution. The inverse will hold for a more cohesive mixture displaying a negative H^{E}. The second term, $\ln \eta(S)$, corresponds to the effect of the excess entropy of the mixture. The third term, $\ln \eta(fv)$, will give a positive contribution to $\Delta \ln \eta_{\text{th}}$ or increase the viscosity of the mixture if there is a contraction on mixing as is the case in systems with a difference in the free volumes between the components. The opposite will be the case if an expansion on mixing occurs. The excess enthalpy H^{E} and excess entropy S^{E}, according to the Flory–Patterson theory [7, 8, 48], are given by

$$H^{\text{E}} = \left(\sum_i x_i P_i^* V_i^* \right) \left\{ \tilde{C}_p \left[\sum_i \psi_i \tilde{T}_i - \tilde{T}_u \right] + \chi_{12} \theta_2 \psi_1 [1/\tilde{v} + \tilde{T}_u \tilde{C}_p] / P_i^* \right\} \tag{18}$$

and

$$S^{\text{E}} = -3 \sum_i \cdot (x_i P_i^* V_i^* / T_i^*) \ln[(\tilde{v}_i^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] \tag{19}$$

Here θ_i and ψ_i represent the surface fraction and contact-energy fraction [49].

The quantities $\tilde{v}$, $\tilde{T}$, and $\tilde{C}_P$ represent the reduced volume, temperature, and configurational heat capacity. P_i^*, V_i^*, and T_i^* are the Flory reduction parameters, and χ_{12} is the contact interaction parameter. The reduced volume $\tilde{v}_u$ for $\tilde{T}_u$ of the mixture is defined as [47]

$$1/\tilde{v}_i = \sum_i \psi_i / \tilde{v}_i \tag{20}$$

The contact interaction parameter χ_{12} is considered as an adjustable parameter and can be obtained from any thermodynamic property. H^{E} is preferred over other thermodynamic properties. The values of Flory's parameters $\tilde{v}$, V_i^*, P_i^*, T_i^*, and the molecular surface-to-volume ratio S used in the theoretical calculations are listed in Table VII. The experimental H^{E} [42, 43, 47], compatible values of the contact interaction parameter χ_{12}, three contributional terms $\ln \eta(H)$, $\ln \eta(S)$, and $\ln \eta(fv)$, the theoretical excess viscosity $\Delta \ln \eta_{\text{th}}$ and the difference δ $(= \Delta \ln \eta_{\text{exp}} - \Delta \ln \eta_{\text{th}})$ at equimolar composition are recorded in Table VIII.

Table VII. Flory Parameters of Pure Components at 303.15 K

Component	$\tilde{v}$	V^* (cm^3·mol^{-1})	P^* (J·cm^{-3})	T^* (K)	S (Å^{-1})
C_6H_6	1.2975	69.76	623	4730	1.00
$C_6H_5CH_3$	1.2677	84.74	543	5055	0.93
$C_6H_5CH_2CH_3$	1.2565	98.42	548	5198	0.95
$C_6H_5CH(CH)_2$	1.2691	111.00	540	5038	0.85
$C_6H_5C(CH_3)_3$	1.2020	130.00	542	6126	0.81
o-$C_6H_4(CH_3)_2$	1.2444	97.40	544	5367	0.95
m-$C_6H_4(CH_3)_2$	1.2538	98.40	562	5234	0.95
p-$C_6H_4(CH_3)_2$	1.2538	99.11	526	5234	0.95

An analysis of Table VIII shows that for benzene + alkylbenzene the enthalpic contribution $\ln \eta_H$ is comparatively large and negative compared to that for alkylbenzene + alkylbenzene. Furthermore, the free volume term is large and positive for mixtures containing TBB compared to the other mixtures. For six systems $C_6H_6 + C_6H_5CH_3$, $C_6H_5CH_3 + C_6H_5CH(CH_3)_2$, $C_6H_5CH_3 + C_6H_5C(CH_3)_3$, $C_6H_5CH_2CH_3 + C_6H_5CH(CH_3)_2$, o-$C_6H_4(CH_3)_2$ + m-$C_6H_4(CH_3)_2$, and o-$C_6H_4(CH_3)_2$ + p-$C_6H_4(CH_3)_2$, the correct sign of $\Delta \ln \eta$ is predicted by the PFPBD theory while for the other mixtures the opposite sign is predicted. The last column in Table VIII shows that the difference δ between experimental and predicted values of $\Delta \ln \eta$ for the present mixtures varies from −0.012 to 0.058. Except for $C_6H_6 + C_6H_5CH_3$,

Table VIII. Values of the Experimental H^E, Flory's Interaction Parameter χ_{12}, Terms $\ln \eta_H$, $\ln \eta_S$, $\ln \eta_{fv}$, $\Delta \ln \eta_{th}$, and Difference $\delta(= \Delta \ln \eta_{exp} - \Delta \ln \eta_{th})$ at 303.15 K

Mixture	$H^{E\,a}$ (J·mol^{-1})	χ_{12} (J·cm^{-3})	$\ln \eta_H$	$\ln \eta_S$	$\ln \eta_{fv}$	$\Delta \ln \eta_{th}$	δ
$C_6H_6 + C_6H_5CH_3$	69	3.76	−0.027	0.003	−0.009	−0.033	0.029
$C_6H_6 + C_6H_5CH_2CH_3$	98	5.07	−0.039	0.002	0.005	−0.032	0.039
$C_6H_6 + C_6H_5CH(CH)_2$	111	5.47	−0.044	0.007	0.011	−0.025	0.047
$C_6H_6 + C_6H_5C(CH_3)_3$	120	7.98	−0.048	−0.048	0.076	−0.020	0.043
$C_6H_5CH_3 + C_6H_5CH_2CH_3$	−9	−0.37	0.004	−0.001	0.006	0.008	−0.010
$C_6H_5CH_3 + C_6H_5CH(CH_3)_2$	−14	−0.60	0.006	−0.001	0.000	0.004	0.016
$C_6H_5CH_3 + C_6H_5C(CH_3)_3$	−10	0.70	0.004	−0.032	0.071	0.043	−0.012
$C_6H_5CH_2CH_3 + C_6H_5CH(CH_3)_2$	7	0.31	−0.003	0.000	−0.007	−0.010	0.009
$C_6H_5CH(CH_3)_2 + C_6H_5C(CH_3)_3$	−12	1.48	−0.005	−0.037	−0.012	−0.053	0.058
o-$C_6H_4(CH_3)_2$ + m-$C_6H_4(CH_3)_2$	11	0.46	−0.004	0.000	−0.004	−0.008	0.004
m-$C_6H_4(CH_3)_2$ + p-$C_6H_4(CH_3)_2$	−8	−0.30	0.003	−0.001	0.000	0.003	−0.002
o-$C_6H_4(CH_3)_2$ + p-$C_6H_4(CH_3)_2$	6.4	0.25	−0.003	0.000	−0.001	−0.003	−0.008

[a] From Refs. 26, 27, and 31.

$C_6H_6 + C_6H_5CH_2CH_3$, $C_6H_6 + C_6H_5CH(CH_3)_2$, $C_6H_6 + C_6H_5C(CH_3)_3$, and $C_6H_5CH(CH_3)_2 + C_6H_5C(CH_3)_3$, the values of δ are very small.

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