International Journal of Thermophysics, Vol. 15, No. 4, 1994

Viscosity of Nonelectrolyte Liquid Mixtures. III. Binary Mixtures of Methyl Methacrylate with Hydrocarbons, Haloalkanes, and Alkylamines

S. L. Oswal,[1,2] **B. M. Patel,**[1], **H. R. Shah,**[1] **and P. Oswal**[3]

Received March 28, 1994

Measurements of the viscosity η and the density ρ are reported for 14 binary mixtures of methyl methacrylate (MMA) with hydrocarbons, haloalkanes, and alkylamines at 303.15 K. The viscosity data have been correlated with equations of Grunberg and Nissan, of McAllister, and of Auslaender. Furthermore, excess viscosity $\Delta \ln \eta$ and excess Gibbs energy of activation ΔG^{*E} of viscous flow have been calculated and have been used to predict molecular interactions occurring in present binary mixtures. The results show the existence of specific interactions in MMA + aromatic hydrocarbons, MMA + haloalkanes, and MMA + primary amines.

KEY WORDS: Alkylamine; aromatic hydrocarbons; binary liquid mixtures; cyclohexane; density; Gibbs energy of activation; haloalkanes; *n*-hexane; molecular interactions; viscosity.

1. INTRODUCTION

Polymerization of methyl methacrylate (MMA) leads to an important synthetic polymer which is an excellent substitute for glass, besides having many other applications [1-3]. This monomer has also been widely used for grafting onto wool, silk, and nylon fiber [4-6]. The production of methyl acrylate esters of higher alcohols by an ester interchange reaction between MMA and the alcohol is usually carried out in other solvents [7, 8]. Therefore, the knowledge of thermodynamic, acoustic, and transport properties of the mixtures of MMA in different types of solvents is

---

[1] Department of Chemistry, South Gujarat University, Surat 395007, India.

[2] To whom correspondence should be addressed.

[3] Department of Chemistry, Government College, Pratabgarh 312605, India.

0195-928X/94/0700-0627$07.00/0

useful in the design of an efficient industrial process and for the solution of many problems concerning heat transfer and fluid flow. Such work is equally informative in gaining insight into the structural changes associated with the liquids. It also reveals information about the molecular packing, molecular motion, and various types of molecular interactions as related to size, shape, and chemical nature of the component molecules [9–16]. Looking into these aspects, we considered it fruitful to undertake measurements of viscosity, density, speed of sound, and isentropic compressibility of monomer MMA in a variety of polar and nonpolar solvents. In this paper, we report densities and viscosities at 303.15 K of MMA solutions in 14 solvents of different types and polarities.

2. EXPERIMENTS

The methods and techniques used to determine the viscosity η and the density ρ have been described in previous publications [10, 11, 17]. Measurements of the kinematic viscosity η/ρ were made with a modified Ubbelohde suspended-level viscometer [18]. The viscometer was designed so as to reduce surface tension effects to negligible values [19]. Four or five sets of readings of flow time were taken for each pure liquid or liquid mixture at 303.15 K. The arithmetic mean was taken for the purpose of calculations. The viscometer had been calibrated with doubly distilled water, benzene, and cyclohexane [20]. The densities ρ of pure componenets and the mixtures at 303.15 K required for converting kinematic viscosities into absolute viscosities were measured with an Anton Paar Densimeter (Model DMA 60/602). The temperature was kept constant to within ± 0.02 K. The errors in η and ρ are estimated as 0.002 mPa s and 0.02 kg m^{-3}, respectively.

MMA (BDH, AR) was vigorously shaken several times with a 25% alkali solution. It was washed with distilled water to remove alkali and distilled under reduced pressure in a stream of N_2 [20]. *n*-Hexane (C_6H_{14}) from Fluka AG Puris and cyclohexane (C_6H_{12}), 1-chlorohexane ($C_6H_{13}Cl$), and 1-bromohexane ($C_6H_{13}Br$) from Merck, AR, were dried over a 4A-type molecular sieve (Fluka) and then fractionally distilled. Benzene (C_6H_6), toluene ($C_6H_5CH_3$), and chlorobenzene (C_6H_5Cl) from BDH, AR, were treated with H_2SO_4 till free of thiophene [20]. Then they were washed, dried, and distilled fractionally. *n*-Propylamine ($C_3H_7NH_2$), *n*-butylamine ($C_4H_9NH_2$), and tri-*n*-butylamine [$(C_4H_9)_3N$] from Fluka AG Puris were stored over sodium and fractionally distilled [20, 21]. Carbon tetrachloride (CCl_4) from BDH, AR, was fractionally distilled over P_2O_5. Chloroform ($CHCl_3$) from BDH, AR, was shaken with H_2SO_4 to remove ethanol, then washed with dilute NaOH and ice water. It was dried

Table I. Comparison of Physical Properties of Pure Liquids

	Temp.	Density ($kg \cdot m^{-3}$)		Refractive index	
Liquid	(K)	expt.	Lit.	Expt.	Lit.
MMA	303.15	931.71	931.74 [20]	1.4096	1.4094 [20]
C_6H_{14}	298.15	655.16	654.84 [20]	1.3727	1.3723 [20]
C_6H_{12}	298.15	773.90	773.87 [20] 773.87 [22]	1.4242	1.4235 [20]
C_6H_6	298.15	873.61	873.60 [20] 873.64 [22]	1.4971	1.4979 [20]
$C_6H_5CH_3$	303.15	856.99	857.54 [20]	1.4910	1.4913 [20]
C_6H_5Cl	303.15	1094.69	1095.50 [20]	1.5221	1.5190 [20]
CCl_4	303.15	1574.82	1574.80 [20]	1.4541	1.4546 [20]
$CHCl_3$	303.15	1470.61	1470.60 [20]	1.4410	1.4400 [20]
$C_2H_4Cl_2$	303.15	1238.02	1238.31 [20]	1.4399	1.4394 [20]
$C_2H_2Cl_4$	303.15	1578.09	1578.60 [20] 1578.52 [14]	1.4880	1.4881 [20]
$C_6H_{13}Cl$	298.15	878.18	878.50 [25]	1.4205	1.4199 [25]
$C_6H_{13}Br$	298.15	1174.20	1174.40 [25]	1.4485	1.4478 [25]
$C_3H_7NH_2$	298.15	712.44	712.10 [20]	1.3853	1.3851 [20]
$C_4H_9NH_2$	298.15	733.23	733.10 [21]	1.3997	1.3987 [20]
$(C_4H_9)_3N$	298.15	774.23	773.78 [21] 774.30 [20] 774.60 [24]	1.4267	1.4265 [23] 1.4268 [24]

over anhydrous K_2CO_3 and fractionally distilled. 1,2-dichloroethane ($C_2H_4Cl_2$) from Sisco, India, was treated first with dilute NaOH and then with distilled water. It was dried over anhydrous $CaCl_2$ and distilled over P_2O_5. 1,1,2,2-Tetrachloroethane ($C_2H_2Cl_4$) from Riedel-AG was repeatedly shaken with a K_2CO_3 solution. It was dried over anhydrous K_2CO_3, followed by fractional distillation [14].

The purities of the liquid samples were checked by gas–liquid chromatography and by measuring the density and the refractive index n_D. The measured values of ρ and n_D were found to be in good agreement with reliable literature values [14, 20–25] as shown in Table I.

3. RESULTS

The experimental results obtained for ρ and η for the 14 binary mixtures of MMA with C_6H_{14}, C_6H_{12}, C_6H_6, $C_6H_5CH_3$, C_6H_5Cl, CCl_4, $CHCl_3$, $C_2H_4Cl_2$, $C_2H_2Cl_4$, $C_6H_{13}Cl$, $C_6H_{13}Br$, $C_3H_7NH_2$, $C_4H_9NH_2$, and $(C_4H_9)_3N$ over the entire range of mole fractions at 303.15 K are presented in Tables II to V. The viscosities η in Tables II to V are represented by a polynomial,

$$\eta = \sum_{i=0}^{n} A_i x_1^i \qquad (1)$$

The coefficients A_i obtained from a least-squares fit are given in Table VI, together with the standard deviations σ. No published work on viscosity measurments was found for the present systems with which to compare our results.

Figures 1 and 2 show the dependence of η on x_1, the mole fraction of MMA for all binary mixtures. Figures 1 and 2 reveal that the values of η increase with increases in the mole fraction of MMA for the three mixtures MMA + C_6H_{14}, MMA + $C_3H_7NH_2$, and MMA + $C_4H_9NH_2$, while they decrease for the mixtures MMA + C_6H_{12}, MMA + C_6H_6, MMA + C_6H_5Cl, MMA + CCl_4, MMA + $C_2H_4Cl_2$, MMA + $C_2H_2Cl_4$, MMA + $C_6H_{13}Cl$, and MMA + $(C_4H_9)_3N$. The mixture MMA + $C_6H_5CH_3$ shows almost no variation in viscosity with x_1. Of the remaining two mixtures,

Table II. Density, Viscosity, Excess Viscosity, and Excess Gibbs Energy of Activation for MMA + Saturated Hydrocarbons at 303.15 K

x_1	ρ (kg·m^{-3})	η (mPa·s)	$\Delta \ln \eta$	ΔG^{*E} (J·mol^{-1})
		MMA + C_6H_{14}		
0.0000	650.53	0.2889	—	—
0.1029	672.86	0.2962	−0.0342	−75
0.2077	696.67	0.3069	−0.0595	−130
0.4005	745.10	0.3338	−0.0865	−191
0.5052	773.52	0.3523	−0.0929	−206
0.6046	802.05	0.3758	−0.0856	−189
0.7056	832.66	0.4934	−0.0729	−160
1.0000	931.71	0.5142	—	—
		MMA + C_6H_{12}		
0.0000	769.12	0.8211	—	—
0.1178	783.71	0.6811	−0.1318	−318
0.2021	795.33	0.6254	−0.1777	−428
0.3973	824.62	0.5474	−0.2195	−528
0.4984	840.99	0.5261	−0.2119	−509
0.5963	857.51	0.5188	−0.1800	−431
0.8040	894.64	0.5141	−0.1002	−239
0.9019	913.00	0.5099	−0.0527	−126
1.0000	931.71	0.5142	—	—

only MMA + $CHCl_3$ exhibits a maxima around $x_1 = 0.4$. Though there are no minima or maxima for the mixture MMA + $C_6H_{13}Br$, there is a dip in the graph at a low mole fracton of MMA. The section between 0.45 and 1.0 shows a slight positive deviation.

Figures 1 and 2 also reveal that large and negative deviations from linear dependence on x_1 are observed for MMA + C_6H_{12} and MMA + C_6H_{14}, while small and negative deviations are observed for MMA +

Table III. Density, Viscosity, Excess Viscosity, and Excess Gibbs Energy of Activation for MMA + Aromatic Hydrocarbons at 303.15 K

x_1	ρ ($kg \cdot m^{-3}$)	η ($mPa \cdot s$)	$\Delta \ln \eta$	ΔG^{*E} ($J \cdot mol^{-1}$)
		MMA + C_6H_6		
0.0000	868.20	0.5621	—	—
0.1019	874.60	0.5507	−0.0114	−22
0.1980	881.21	0.5430	−0.0169	−32
0.4005	894.49	0.5273	−0.0282	−56
0.4996	900.51	0.5220	−0.0295	−58
0.5998	906.66	0.5190	−0.0264	−51
0.8001	919.22	0.5141	−0.0180	−35
0.8960	926.00	0.5142	−0.0092	−19
1.0000	931.71	0.5142	—	—
		MMA + $C_6H_5CH_3$		
0.0000	856.99	0.5219	—	—
0.1041	864.83	0.5201	−0.0019	−6
0.2049	872.39	0.5187	−0.0031	−8
0.4069	887.52	0.5163	−0.0047	−12
0.5046	894.82	0.5155	−0.0048	−14
0.6068	902.44	0.5148	−0.0047	−12
0.7980	916.68	0.5141	−0.0032	−8
0.8960	923.97	0.5141	−0.0017	−4
1.0000	931.71	0.5142	—	—
		MMA + C_6H_5Cl		
0.0000	1094.69	0.7134	—	—
0.0990	1078.22	0.6943	0.0053	14
0.1971	1061.81	0.6738	0.0074	18
0.3987	1028.43	0.6345	0.0133	33
0.4982	1012.10	0.6147	0.0142	35
0.6984	979.62	0.5743	0.0118	37
0.7989	963.42	0.5538	0.0083	21
0.8987	947.70	0.5349	0.0061	17
1.0000	931.71	0.5142	—	—

Table IV. Density, Viscosity, Excess Viscosity, and Excess Gibbs Energy of Activation for MMA + Chloroalkanes at 303.15 K

x_1	ρ (kg · m^{-3})	η (mPa · s)	$\Delta \ln \eta$	ΔG^{*E} (J · mol^{-1})
		MMA + CCl_4		
0.0000	1574.82	0.8442	—	—
0.0997	1501.21	0.7954	−0.0101	−19
0.1978	1433.49	0.7530	−0.0163	−32
0.4056	1294.15	0.6767	−0.0201	−38
0.5067	1229.34	0.6410	−0.0241	−49
0.5941	1174.65	0.6167	−0.0195	−39
0.7976	1050.45	0.5599	−0.0152	−32
0.8944	994.76	0.5360	−0.0109	−28
1.0000	931.71	0.5142	—	—
		MMA + $CHCl_3$		
0.0000	1470.61	0.5246	—	—
0.0522	1433.50	0.5364	0.0234	65
0.1301	1380.11	0.5505	0.0508	143
0.3102	1266.68	0.5767	0.1009	282
0.4132	1206.83	0.5808	0.1100	310
0.5161	1150.60	0.5747	0.1015	290
0.7435	1040.20	0.5589	0.0782	222
0.8591	989.30	0.5420	0.0498	141
1.0000	931.71	0.5142	—	—
		MMA + $C_2H_4Cl_2$		
0.0000	1238.02	0.7307	—	—
0.1012	1196.07	0.6868	−0.0264	−52
0.1978	1158.04	0.6544	−0.0408	−76
0.3975	1090.32	0.6068	−0.0461	−89
0.4985	1059.52	0.5867	−0.0443	−76
0.6234	1024.12	0.5632	−0.0413	−73
0.8713	960.79	0.5284	−0.0180	−31
1.0000	931.71	0.5142	—	—
		MMA + $C_2H_2Cl_4$		
0.0000	1578.09	1.5209	—	—
0.0942	1517.32	1.4217	0.0347	86
0.1967	1451.08	1.3168	0.0692	172
0.2785	1398.83	1.2353	0.0940	233
0.4978	1258.29	0.9971	0.1176	289
0.5980	1192.99	0.8879	0.1103	272
0.7131	1117.59	0.7662	0.0877	217
0.9050	992.59	0.5902	0.0348	68
1.0000	931.71	0.5142	—	—

Table IV. *(Continued)*

x_1	ρ (kg·m^{-3})	η (mPa·s)	$\Delta \ln \eta$	ΔG^{*E} (J·mol^{-1})
		MMA + $C_6H_{13}Cl$		
0.0000	868.76	0.6544	—	—
0.1343	874.22	0.6215	−0.0192	−36
0.1947	877.03	0.6053	−0.0311	−61
0.3625	885.17	0.5729	−0.0456	−88
0.4962	892.19	0.5511	−0.0522	−102
0.6029	899.64	0.5375	−0.0575	−101
0.8144	914.92	0.5199	−0.0337	−65
0.8988	922.40	0.5152	−0.0221	−44
1.0000	931.71	0.5142	—	—
		MMA + $C_6H_{13}Br$		
0.0000	1162.64	0.9030	—	—
0.1439	1134.19	0.8087	−0.0293	−57
0.2632	1110.22	0.7611	−0.0227	−32
0.4885	1061.77	0.6895	0.0054	40
0.5904	1038.09	0.6665	0.0288	106
0.6826	1015.81	0.6354	0.0329	114
0.8513	973.16	0.5709	0.0209	71
0.9171	955.58	0.5459	0.0131	43
1.0000	931.71	0.5142	—	—

C_6H_6, MMA + CCl_4, MMA + $C_2H_4Cl_2$, MMA + $C_6H_{13}Cl$, and MMA + $(C_4H_9)_3N$. For the mixtures MMA + $CHCl_3$, MMA + $C_3H_7NH_2$, and MMA + $C_4H_9NH_2$, the deviations are small but positive. The η for MMA + C_6H_5Cl, MMA + $C_6H_5CH_3$, and MMA + $C_2H_2Cl_4$ varies almost-linearly with the x_1. For the mixture MMA + $C_6H_{13}Br$, though small, both negative and positive deviations are observed.

Qunatitatively, the deviations of the viscosities from the ideal mixture values can be calculated from the Arrhenius equation,

$$\Delta \ln \eta = \ln(\eta/\eta_2^0) - x_1 \ln(\eta_1^0/\eta_2^0) \tag{2}$$

where η_i^0 represent the viscosities of pure component i. The values of the excess viscosity $\Delta \ln \eta$, given in Tables II to V, column 4, have been fitted to a Redlich–Kister [26] polynomial,

$$\Delta \ln \eta = x_1 x_2 \sum B_i (1 - 2x_1)^{i-1} \tag{3}$$

The coefficients B_i in Eq. (3), obtained by the method of least squares with all points weighted equally, and the standard deviations σ are given in Table VII.

The dependence of $\Delta \ln \eta$ on the mole fraction x_1 of MMA is shown in Figs. 3 and 4. Figures 3 and 4 show that the observed values of $\Delta \ln \eta$ are large and negative for MMA + C_6H_{12} and MMA + C_6H_{14}; comparatively small and negative for MMA + C_6H_6, MMA + $C_6H_5CH_3$, MMA + CCl_4, MMA + $C_2H_4Cl_2$, and MMA + $C_6H_{13}Cl$; small and positive for MMA + C_6H_5Cl, MMA + $C_4H_9NH_2$, and MMA + $(C_4H_9)_3N$; and large and

Table V. Density, Viscosity, Excess Viscosity, and Excess Gibbs Energy of Activation for MMA + Amines at 303.15 K

x_1	ρ (kg · m^{-3})	η (mPa · s)	$\Delta \ln \eta$	ΔG^{*E} (J · mol^{-1})
		MMA + $C_3H_7NH_2$		
0.0000	707.55	0.3468	—	—
0.1506	750.60	0.3820	0.0374	100
0.3776	807.30	0.4355	0.0790	214
0.5053	836.28	0.4623	0.0884	238
0.6058	857.83	0.4809	0.0884	237
0.8285	901.58	0.5081	0.0556	148
1.0000	931.71	0.5142	—	—
		MMA + $C_4H_9NH_2$		
0.0000	729.43	0.4430	—	—
0.1016	750.75	0.4525	0.0061	18
0.1939	771.11	0.4608	0.0105	27
0.3316	801.03	0.4724	0.0148	34
0.4989	835.73	0.4852	0.0166	38
0.5966	855.15	0.4921	0.0162	37
0.8001	894.72	0.5045	0.0107	24
0.9006	913.78	0.5097	0.0060	13
1.0000	931.71	0.5142	—	—
		MMA + $(C_4H_9)_3N$		
0.0000	770.45	1.1553	—	—
0.2100	787.36	0.9849	0.0105	142
0.3945	805.74	0.8491	0.0114	214
0.4886	816.88	0.7874	0.0123	235
0.6041	833.08	0.7144	0.0084	231
0.7985	870.75	0.6078	0.0041	171
1.0000	931.71	0.5142	—	—

Table VI. Coefficients A_i of Eq. (1) for the Viscosity of Binary Mixtures MMA (1) + Component 2 at 303.15 K in mPa·s

Component 2	A_1	A_2	A_3	A_4	A_5	σ
C_6H_{14}	0.2909	−0.0043	0.2272	—	—	0.0020
C_6H_{12}	0.8200	−1.4239	0.2642	−2.3228	0.7991	0.0038
C_6H_6	0.5618	−0.1104	0.0637	—	—	0.0008
$C_6H_5CH_3$	0.5205	−0.0077	—	—	—	0.0011
C_6H_5Cl	0.7136	−0.1994	—	—	—	0.0004
CCl_4	0.8418	−0.4638	0.1369	—	—	0.0019
$CHCl_3$	0.5237	0.2651	−0.3492	0.0749	—	0.0022
$C_2H_4Cl_2$	0.7289	−0.4322	0.3577	−0.1415	—	0.0024
$C_2H_2Cl_4$	1.5181	−0.9521	−0.3482	0.2956	—	0.0034
$C_6H_{13}Cl$	0.6548	−0.2756	0.1346	—	—	0.0008
$C_6H_{13}Br$	0.9030	−0.8357	1.5018	−1.6736	0.6181	0.0026
$C_3H_7NH_2$	0.3436	0.2974	−0.1241	−0.1203	—	0.0004
$C_4H_9NH_2$	0.4428	0.0984	−0.0269	—	—	0.0002
$(C_4H_9)_3N$	1.1556	−0.8631	0.2216	—	—	0.0007

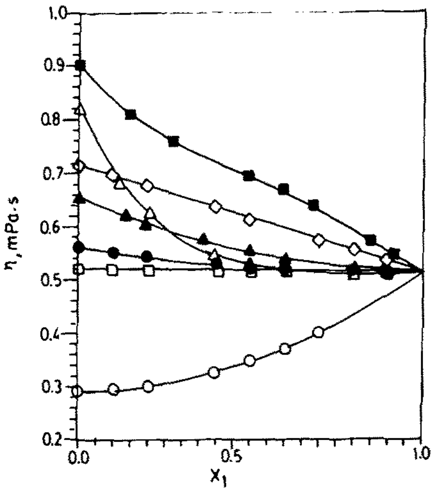

Fig. 1. Dependence of viscosity η at 303.15 K on mole fraction x_1 of MMA for binary mixtures of MMA with C_6H_{14} (○), C_6H_{12} (△), C_6H_6 (●), $C_6H_5CH_3$ (□), C_6H_5Cl (◇), $C_6H_{13}Cl$ (▲), and $C_6H_{13}Br$ (■). Solid line represents Eq. (1).

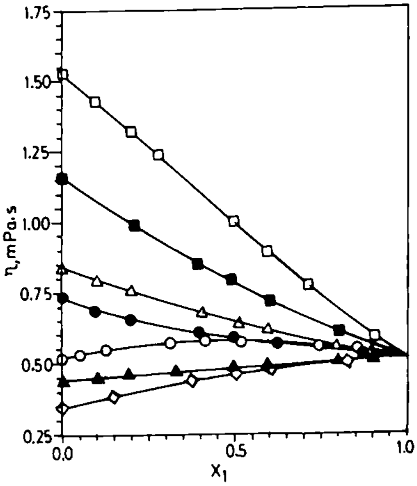

Fig. 2. Dependence of viscosity η at 303.15 K on mole fraction x_1 of MMA for binary mixtures of MMA with CCl_4 (△), $CHCl_3$ (○), $C_2H_4Cl_2$ (●), $C_2H_2Cl_4$ (□), $C_3H_7NH_2$ (◇), $C_4H_9NH_2$ (▲), and $(C_4H_9)_3N$ (■). Solid line represents Eq. (1).

Table VII. Coefficients B_i of Eq. (3) for Excess Viscosity of Binary Mixtures MMA (1) + Component 2 at 303.15 K

Component 2	B_1	B_2	B_3	σ
C_6H_{14}	−0.3625	−0.0162	0.0146	0.0016
C_6H_{12}	−0.8271	−0.4184	−0.1671	0.0039
C_6H_6	−0.1125	−0.0089	—	0.0012
$C_6H_5CH_3$	−0.0194	—	—	0.0001
C_6H_5Cl	0.0560	−0.0040	—	0.0008
CCl_4	−0.0854	−0.0011	−0.0427	0.0017
$CHCl_3$	0.4337	0.0406	—	0.0040
$C_2H_4Cl_2$	−0.1804	−0.0780	−0.0741	0.0018
$C_2H_2Cl_4$	0.4663	0.0112	−0.0927	0.0023
$C_6H_{11}Cl$	−0.2072	−0.0364	—	0.0014
$C_6H_{13}Br$	0.0562	−0.2890	−0.1777	0.0043
$C_3H_7NH_2$	0.3497	−0.0732	—	0.0012
$C_4H_9NH_2$	0.0670	—	—	0.0001
$(C_4H_9)_3N$	0.0449	0.0320	—	0.0008

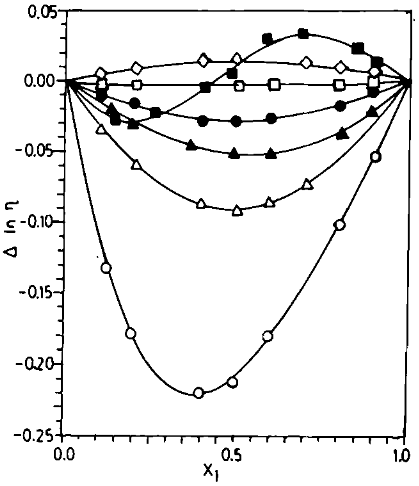

Fig. 3. Dependence of excess viscosity $\Delta \ln \eta$ on mole fraction x_1 of MMA for binary mixtures at 303.15 K. Symbols C_6H_{14} (○), C_6H_{12} (△), C_6H_6 (●), $C_6H_5CH_3$ (□), C_6H_5Cl (◇), $C_6H_{13}Cl$ (▲), and $C_6H_{13}Br$ (■). Solid line represents Eq. (3).

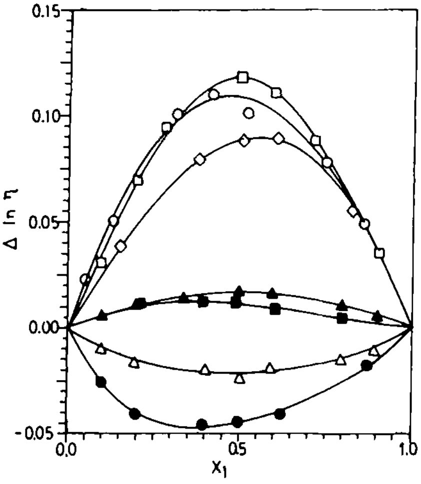

Fig. 4. Dependence of excess viscosity $\Delta \ln \eta$ on mole fraction x_1 of MMA for binary mixtures at 303.15 K. Symbols as in the legend to Fig. 2. Solid line represents Eq. (3).

positive for MMA + $CHCl_3$, MMA + $C_2H_2Cl_4$, and MMA + $C_3H_7NH_2$. For MMA + $C_6H_{13}Br$ both positive and negative $\Delta \ln \eta$ are observed—negative when $x_1 < 0.3$, positive otherwise.

4. CORRELATING EQUATIONS

There are currently increasing demands for the accuracy of predicting liquid-mixture viscosity for industrial applications. Therefore, it is desirable to have equations that are predictive in nature. The viscosities of liquid mixtures in terms of pure-component data have been correlated by many investigators [27–29]. In this work, the Grunberg–Nissan [32], McAllister [30]; and Auslaender [31] equations have been employed to correlate the present viscosity results.

The Grunberg–Nissan equation [32]

$$\ln \eta = x_1 \ln \eta_1^0 + x_2 \ln \eta_2^0 + x_1 x_2 G_{12} \tag{4}$$

gave the best overall fit among the 25 single-parameter equations tested for representing the viscosities of a large number of binary systems [27].

We analyze Eq. (4) in two ways: (i) by calculating G_{12} for each of the binary mixtures at each individual composition and (ii) by calculating one optimum value of G_{12} for each binary mixtures using all the experimental points.

The McAllister equation [31] based on Eyring's theory of absolute reaction rates and three-body interaction model is

$$\begin{aligned} \ln \nu = {} & x_1^3 \ln \nu_1^0 + 3x_1^2 x_2 \ln Z_{12} + 3x_1 x_2^2 \ln Z_{21} + x_2^3 \ln \nu_2^0 \\ & - \ln(x_1 + x_2 M_2/M_1) + 3x_1^2 x_2 \ln(\tfrac{2}{3} + M_2/3M_1) \\ & + 3x_1 x_2^2 \ln(\tfrac{1}{3} + 2M_2/3M_1) + x_2^3 \ln(M_2/M_1) \end{aligned} \tag{5}$$

where Z_{12} and Z_{21} are interaction parameters and M_i and ν_i^0 are the molecular mass and kinematic viscosity of pure component i.

A three-parameter equation, due to Auslaender [32], has the form

$$x_1(x_1 + B_{12}x_2)(\eta - \eta_1^0) + A_{21}(B_{21}x_1 + x_2)(\eta - \eta_2^0) = 0 \tag{6}$$

where B_{12}, B_{21}, and A_{21} are the parameters representing binary interactions.

The results of the three correlating equations, Eqs. (4)–(6), are compiled in Table VIII. In Table VIII, the second column provides G_{12} of Eq. (4) and the fourth and fifth columns list Z_{12} and Z_{21} of Eq. (5), while the seventh to ninth columns present the values of B_{12}, B_{21}, and A_{21} of Eq. (6). The values of the different parameters listed in Table VIII were

Table VIII. Least-Squares Parameters of Eqs. (4) to (6) with Percentage Standard Deviations $\sigma(\%)$ for MMA (1) + Component 2 Mixtures at 303.15 K

Component 2	G_{12}	$\sigma(\%)$	Z_{12}	Z_{21}	$\sigma(\%)$	B_{12}	A_{21}	B_{21}	$\sigma(\%)$
C_6H_{14}	−0.357	0.95	0.476	0.406	0.71	—	—	—	—
C_6H_{12}	−0.866	3.10	0.597	0.564	0.67	1.004	0.196	−0.484	0.38
C_6H_6	−0.110	0.16	0.564	0.591	0.14	−0.164	−0.031	−5.289	1.04
C_6H_5Cl	0.056	0.07	0.594	0.656	0.66	0.161	−0.164	−6.157	0.06
$C_6H_5CH_3$	−0.020	0.01	0.566	0.585	0.01	−2.151	−0.899	−0.272	0.01
CCl_4	−0.106	0.39	0.520	0.515	0.40	−0.222	−0.135	−4.656	0.77
$CHCl_3$	0.451	1.05	0.538	0.503	0.60	−19.294	0.568	38.277	0.79
$C_2H_4Cl_2$	−0.209	0.68	0.552	0.537	0.35	−0.285	−0.131	−3.646	0.91
$C_2H_2Cl_4$	0.431	0.59	0.742	0.897	0.54	−0.463	−0.412	−2.062	1.52
$C_6H_{13}Cl$	−0.202	0.33	0.573	0.649	0.30	0.619	0.363	0.456	0.46
$C_6H_{13}Br$	0.034	2.52	0.678	0.619	0.91	0.369	0.076	13.970	0.50
$C_3H_9NH_2$	0.360	0.89	0.603	0.545	0.57	1.119	0.857	0.062	0.54
$C_4H_9NH_2$	0.067	0.01	0.574	0.596	0.06	1.128	0.954	0.625	0.01
$(C_4H_9)_3N$	0.044	0.33	0.851	1.149	0.20	0.304	0.246	2.711	0.13

obtained from the experimental viscosity data with the method of least squares, assigning equal weights to each point.

The calculated values of G_{12} in Eq. (4) as a function of composition x_1 for each of the mixtures are plotted in Figs. 5 and 6. In general, G_{12} varies with the composition for most of the mixtures.

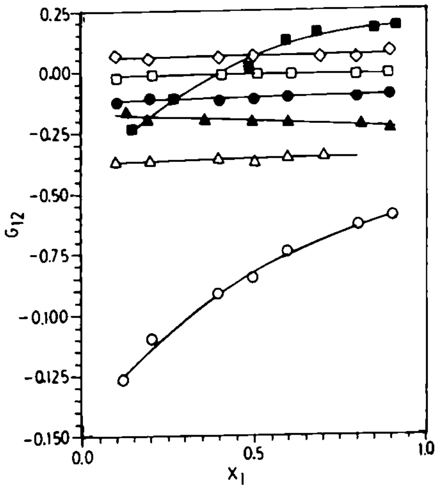

Fig. 5. Variation of Grunberg–Nissan parameter G_{12} of Eq. (4) with mole fraction x_1 of MMA in binary mixtures at 303.15 K. Symbols as in the legend to Fig. 3.

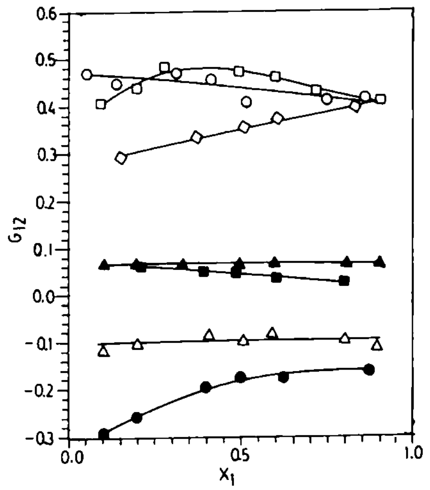

Fig. 6. Variation of Grunberg-Nissan parameter G_{12} of Eq. (4) with mole fraction x_1 of MMA in binary mixtures at 303.15 K. Symbols as in the legend to Fig. 2.

Furthermore, the correlating ability of each of the equations, Eqs. (4) to (6), is tested by calculating the standard percentage deviations $\sigma(\%)$ between the experimental and the calculated viscosity as

$$\sigma(\%)=\left[\frac{1}{n-k}\left\{\frac{100(\eta_{\mathrm{exp}}-\eta_{\mathrm{cal}})}{\eta_{\mathrm{exp}}}\right\}^{2}\right]^{1/2} \tag{7}$$

where n represents the number of data points and k the number of numerical coefficients in respective equations. The values of the standard percentage deviations for each of the equations are also given in Table VIII. The values of σ are in the range from 0.01 to 1.05% for Eq. (4) for the present mixtures except for MMA + C_6H_{12} and MMA + $C_6H_{13}Br$. For the latter mixtures, the values of σ are quite large, i.e., 2.51 and 3.10%, respectively. The σ values are from 0.01 to 0.91% for Eq. (5) and from 0.01 to 1.52% for Eq. (6). The average values of σ for Eqs. (4), (5), and (6) are 0.79 ± 0.93, 0.44 ± 0.27, and 0.55 ± 0.45. From this study, it can be said that the correlating ability decreases in the order McAllister > Auslaender > Grunberg–Nissan.

5. ACTIVATION ENERGY OF VISCOUS FLOW

On the basis of the theory of absolute reaction rates, the excess Gibbs energy of activation ΔG^{*E} of viscous flow may be calculated from [33]

$$\Delta G^{*E}/RT = [\ln(\eta V/\eta_2^0 V_2^0) - x_1 \ln(\eta_1^0 V_1^0/\eta_2^0 V_2^0)] \tag{8}$$

where η and V are the viscosity and molar volume of the mixture, and η_i^0 and V_i^0 are the viscosity and molar volume of the pure component i, respectively. These results are also included in the last column in Tables II to V. The estimated accuracy of ΔG^{*E} is about 20 J mol $^{-1}$. A polynomial of the type given in Eq. (3) was fitted to the $\Delta G^{*E}/RT$ results of each mixture. The values of coefficients B_i and the standard deviations σ are presented in Table IX. The plots of the results of ΔG^{*E} for a few systems and their representation by Eq. (3) are shown in Fig. 7.

Like $\Delta \ln \eta$, the values of ΔG^{*E} are large and negative for MMA + C_6H_{12} and MMA + C_6H_{14}; small and negative for MMA + C_6H_6, MMA + $C_6H_5CH_3$, MMA + CCl_4, MMA + $C_2H_4Cl_2$, and MMA + $C_6H_{13}Cl$; small and positive for MMA + C_6H_5Cl, and MMA + $C_4H_9NH_2$; and large and positive for MMA + $CHCl_3$, MMA + $C_2H_2Cl_4$, MMA + $C_3H_7NH_2$, and MMA + $(C_4H_9)_3N$. For the mixture MMA + $C_6H_{13}Br$ both small negative and small positive values of ΔG^{*E} are observed.

Table IX. Coefficient B_i of Eq. (3) of Binary Mixtures MMA (1) + Component 2 for $\Delta G^{*E}/RT$

Component 2	B_1	B_2	B_3	B_3	σ
C_6H_{14}	−0.3178	−0.0150	0.0190	—	0.0017
C_6H_{12}	−0.7872	−0.4043	−0.1627	—	0.0038
C_6H_6	−0.0874	0.0044	—	—	0.0010
$C_6H_5CH_3$	−0.0205	—	—	—	0.0003
C_6H_5Cl	0.0572	0.0064	—	—	0.0011
CCl_4	0.0660	0.0151	−0.0478	—	0.0021
$CHCl_3$	0.4857	0.0398	—	—	0.0038
$C_2H_4Cl_2$	−0.1238	−0.0690	−0.0711	—	0.0019
$C_2H_2Cl_4$	0.4559	0.0080	0.0802	—	0.0025
$C_6H_{13}Cl$	−0.1599	−0.0324	—	—	0.0014
$C_6H_{13}Br$	0.1007	−0.2413	−0.1455	0.1099	0.0053
$C_3H_7NH_2$	0.3722	−0.0757	—	—	0.0018
$C_4H_9NH_2$	0.0635	−0.0010	—	—	0.0008
$(C_4H_9)_3N$	0.3748	−0.0695	—	—	0.0013

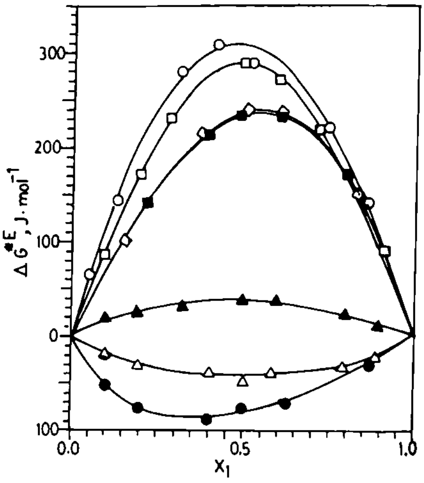

Fig. 7. Dependence of excess Gibbs energy of activation ΔG^{*E} of viscous flow on mole fraction x_1 of MMA in binary mixtures at 303.15 K. Symbols as in the legend to Fig. 2. Solid line represents Eq. (3).

6. MOLECULAR INTERACTIONS

6.1. MMA + Saturated Hydrocarbons

The large and negative values of $\Delta \ln \eta$, ΔG^{*E}, and G_{12} for MMA + C_6H_{12} and MMA + C_6H_{14} are due to disruption of the local dipolar order in MMA by the addition of either C_6H_{12} or C_6H_{14} molecules. The relatively larger negative values of ΔG^{*E} for the cyclohexane mixture than for the *n*-hexane mixture further indicate that cyclohexane is a better order breaker than *n*-hexane [34].

6.2. MMA + Aromatic Hydrocarbons

When cyclohexane is replaced by aromatic hydrocarbon liquids such as C_6H_6, $C_6H_5CH_3$, and C_6H_5Cl, the large and negative values of $\Delta \ln \eta$, ΔG^{*E}, and G_{12} reduce to either small and negative or small and positive values. This suggests the balance of opposite forces in the MMA + aromatic hydrocarbon mixtures. The dispersion interactions are counterbalanced by the specific interactions between the MMA and the aromatic hydrocarbons. The results for excess volumes of these mixtures

[40] also support this observation. Similar, specific interactions were observed for alkyl acetate + aromatic hydrocarbons [10, 35].

6.3. MMA + Haloalkanes

The small and negative values of $\Delta \ln \eta$ and ΔG^{*E} for MMA + CCl_4, MMA + $C_2H_4Cl_2$, and MMA + $C_6H_{13}Cl$ and large and positive values of MMA + $CHCl_3$ and MMA + $C_2H_2Cl_4$ can be attributed to the specific interactions between the unlike components.

The specific interactions of MMA with either CCl_4, $C_6H_{13}Cl$, or $C_6H_{13}Br$ can be visualized as an electron donor and acceptor type. The MMA molecules act as the lone pair electron donor and the haloalkane as the acceptor. In the case of MMA + $CHCl_3$, the large and positive values of ΔG^{*E} (Fig. 7) can be explained by considering H-bond formation between MMA + $CHCl_3$. The present results for MMA + $C_2H_4Cl_2$ and MMA + $C_2H_2Cl_4$ (Fig. 7) can be explained in a similar manner; but apart from H-bonding, the $O \cdots Cl$ interaction in the latter two mixtures is not less significant. Similar results were obtained for acetone mixtures with tetrachloroethylene, methylene chloride, and 1,2-dichloroethane by Nath and Dixit [36].

6.4. MMA + Alkylamines

The positive values of $\Delta \ln \eta$ and ΔG^{*E}, whether small or large, for all three present mixtures of MMA with alkylamines are definitely due to the specific interactions between unlike pairs. In the case of MMA + $C_3H_7NH_2$ and MMA + $C_4H_9NH_2$ mixtures, the specific interactions may involve H-bond formation between oxygen of MMA and H_- of primary amines. However, in the case of MMA + $(C_4H_9)_3N$, the large and positive values of ΔG^{*E} (Fig. 7) may be due partly to the large size difference between the two components of the mixture in addition to the dipole–dipole interactions [21, 37–39].

7. CONCLUSIONS

From the present study, it can be concluded that specific interactions exist in MMA + aromatic hydrocarbons, MMA + haloalkanes, and MMA + primary amines mixtures, whereas the addition of the saturated hydrocarbons cyclohexane and hexane to MMA disrupts the dipolar association present in the MMA molecules.

ACKNOWLEDGMENTS

The authors wish to thank the Head of the Department of Statistics and the Head of the Department of Mathematics for providing the computation facilities.

REFERENCES

1. C. E. Schildknecht, *Vinyl and Related Polymers* (Wiley, New York, 1977).
2. A. M. Usmani, *J. Macromol. Sci.-Chem.* **A20(1)**:61 (1983)
3. J. M. Mays and N. Hadjichristidis, *Rev. Macromol. Chem. Phys.* **C28(3/4)**:371 (1988)
4. G. N. Richards, *J. Appl. Polym. Sci.* **5**:545 (1961).
5. B. N. Misra, I. K. Mehta, and Dogra, *J. Macromol. Sci.-Chem.* **A12(10)**:1513 (1978).
6. B. N. Misra, I. Kaur, and B. Kappor, *Polym. Sci. Contemp. Themes* **1**:377 (1991).
7. T. Tsuruta, T. Makimoto, and H. Kanai, *J. Macromol. Sci.* **1**:31 (1966).
8. N. Hadjichristidis and L. J. Fetters, *Macromolecules* **17**:2303 (1984).
9. R. J. Fort and W. R. Moore, *Trans. Faraday Soc.* **61**:2101 (1965); **62**:1112 (1966).
10. S. L. Oswal, *Can. J. Chem.* **66**:111 (1988).
11. S. L. Oswal and R. P. Phalak, *Int. J. Thermophys.* **13**:251 (1992).
12. S. L. Oswal and J. P. Dave, *Int. J. Thermophys.* **13**:943 (1992).
13. O. Kiyohara and K. Arakawa, *Bull. Chem. Soc. Jap.* **43**:1224, 3037 (1970).
14. J. Nath and A. D. Tripathi, *J. Chem. Eng. Data* **28**:262 (1983).
15. S. L. Oswal and I. N. Patel, *Ind. J. Chem. Sec. A* **29**:870 (1990).
16. J. S. Rowlinson and F. L. Swinton, *Liquid and Liquid Mixtures*, 3rd ed. (Butterworths, London, 1981).
17. S. G. Patel and S. L. Oswal, *J. Chem. Soc. Faraday Trans.* **88**:2497 (1992).
18. L. Ubbelohde, *Ind. Eng. Chem. Anal. Edn.* **9**:85 (1937).
19. F. A. Conçalves, J. Kestin, and J. V. Sengers, *Int. J. Thermophys.* **12**:1013 (1991).
20. J. A. Riddick, W. B. Bunger, and T. K. Sakano, *Organic Solvents Physical Properties and Methods of Purifications*, 4th ed. (Wiley, New York, 1986).
21. T. M. Letcher and J. W. Bayles, *J. Chem. Eng. Data* **16**:266 (1971).
22. K. Tamura, K. Ohomura, and S. Murakami, *J. Chem. Thermodyn.* **15**:859 (1983).
23. C. Klufter, S. Paljk, and D. Krenser, *J. Inorg. Nucl. Chem.* **37**:1729 (1975).
24. R. Philippe, G. Delmas, and M. Couchen, *Can. J. Chem.* **56**:370 (1978).
25. R. C. Weast, *Hand Book of Chemistry and Physics*, 59th ed. (The Chemical Rubber Co., Cleveland, OH, 1979).
26. O. Redlich and A. T. Kister, *Ind. Eng. Chem.* **40**:345 (1948).
27. J. B. Irving, *Viscosity of Liquid Mixtures*, NEL Report Nos. 630 and 631 (National Engineering Laboratory, East Kilbride, Glasgow, 1977).
28. P. Skubla, *Coll. Czech. Chem. Comm.* **46**:303 (1981).
29. R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed. (McGraw-Hill, New York, 1987).
30. P. A. McAllister, *AIChE J.* **6**(3):427 (1960).
31. G. Auslaender, *Brit. Chem. Eng.* **9**:610 (1964).
32. L. Grunberg and A. H. Nissan, *Trans. Faraday Soc.* **45**:125 (1949).
33. S. Glasstones, K. J. Laidler, and H. Eyring, *The Theory of Rate Process* (McGraw-Hill, New York, 1941).
34. S. N. Bhattacharya and D. Patterson, *J. Soln. Chem.* **9**:247 (1980).

35. S. L. Oswal and M. V. Rathnam, *Can. J. Chem.* **62**:2851 (1984).
36. J. Nath and A. P. Dixit, *J. Chem. Eng. Data* **29**:313 (1984).
37. S. L. Oswal and A. V. Rao, *Indian J. Chem. Sec. A* **24**:1024 (1985).
38. S. L. Oswal and A. T. Patel, *Int. J. Thermophys.* **12**:821 (1991).
39. H. Phuong-Nguyen and G. Delmas, *Can. J. Chem.* **64**:681 (1986).
40. B. N. Patel, Ph.D. thesis (South Gujarat University, Surat, India, 1992).