Thermodynamics of acrylic ester–organic solvent mixtures II. Viscosities of mixtures of methyl methacrylate, ethyl methacrylate or butyl methacrylate with *n*-hexane, *n*-heptane, carbon tetrachloride, chlorobenzene or *o*-dichlorobenzene at 303.15 K

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Abstract

The viscosities of fourteen binary mixtures of methyl methacrylate (MMA), ethyl methacrylate (EMA) or butyl methacrylate (BMA) with *n*-hexane, *n*-heptane, carbon tetrachloride, chlorobenzene or *o*-dichlorobenzene were measured at 303.15 K. The mixture viscosities were found to correlate reasonably well with the Grunberg–Nissan, Heric, McAllister and Auslaender equations. The dependence of the derived viscosity deviations both on the size of the alkyl chain in the ester molecules and on the nature of the second component revealed the complex nature of the interactions in these mixtures. The equimolar mixture viscosities of MMA-containing mixtures were analysed by the Bloomfield–Dewan approach on the basis of Flory free-volume theory and the thermodynamic contributions, viz. enthalpy, entropy and free volume terms, were evaluated. The results of the analysis show that dispersing interactions are predominant in the aliphatic hydrocarbon- and carbon tetrachloride-containing mixtures, while both specific and dispersing interactions were found to contribute equally in binary mixtures of MMA and chlorobenzenes.

Keywords: Acrylic esters; Aliphatic hydrocarbons; Chlorobenzenes; Molecular interactions; Thermodynamic contributions

1. Introduction

Acrylic esters are important industrial chemicals and are precursors in the production of technically important homo-, block- and graft copolymers. Thermodynamic

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investigations involving binary mixtures containing acrylic esters and other polar
or non-polar solvents are expected to yield useful information, which can be helpful
in designing efficient industrial processes involving either the production of the
derivatives of the former or their separation. Despite their wide use, binary mixtures
of acrylic esters with other solvents have seldom been studied, in contrast
with numerous reports on the thermodynamic properties of alkyl alkanoate-contain-
ing mixtures. Kehiaian et al. [1] have reviewed measurements of liquid–vapour and
liquid–liquid equilibria, excess enthalpies and activity coefficients of n-alkanoate–n-
alkane and n-alkanoate–n-alkanoate mixtures. The authors have also analysed
the data through a quasi-chemical group contribution model. Ortega and coworkers
[2–8] have recently carried out systematic investigations on several methyl ester–
alkane mixtures through measurements of excess enthalpies and excess volumes.
The excess enthalpies of alkyl ester–1-chloroalkane mixtures were also reported by
the same authors [9]. The excess enthalpies and excess volumes of mixtures of methyl
methacrylate with n-hexane, n-heptane, cyclopentane and cyclohexane were also
reported by Luo et al. [10,11]. Though the majority of studies invloved measurements
of excess volumes, excess enthalpies, vapour–liquid equilibria and vapour–vapour
equilibria, the estimation of other physical properties viz. viscosity, sound velocities
and dielectric constants and the excess functions derived therefrom is also expected to
provide insight into the nature and magnitude of the types of interaction in these
mixtures.

This work is a part of our systematic investigations of various thermodynamic
properties on binary mixtures containing acrylic esters as one of the components. The
excess volumes, isentropic compressibilities and viscosity functions of methyl metha-
crylate–alcohol mixtures have already been reported by us [12,13]. We have recently
communicated the excess volumes and isentropic compressibilities of several mixtures
of alkyl methacrylates with organic solvents [14]. This paper presents viscosity
measurements on binary mixtures of MMA, EMA of BMA with n-hexane, n-heptane,
carbon tetrachloride, chlorobenzene or o-dichlorobenzene at 303.15 K. The measured
viscosities are correlated with several equations. The Bloomfield–Dewan approach
based on Flory free-volume theory is also employed to ascertain the dominant
thermodynamic factor responsible for the observed viscosities of the mixtures.

2. Experimental

2.1. Materials

The acrylic esters MMA, EMA and BMA and the organic solvents n-hexane,
n-heptane, carbon tetrachloride, chlorobenzene and o-dichlorobenzene were the same
as described elsewhere [14]. The absolute viscosities of the pure and mixture compo-
nents were measured with an Ubbelhode suspended level viscometer. Our experimental
values of viscosities of the pure liquids at 303.15 K, along with selected literature values
for comparison, are given in Table 1. It can be seen from the table that our values agree
closely with the literature values.

Table 1
Comparison of viscosities of pure liquids at 303.15 K

Liquid	Viscosity/(mPa s)	
	Exp.	Lit.
MMA	0.5291	0.5142 [15]
EMA	0.5563	–
BMA	0.8508	–
n-Hexane	0.2830	0.2831 [16]
n-Heptane	0.3760	0.3707 [16]
Carbon tetrachloride	0.8450	0.8450 [17]
		0.8442 [15]
Chlorobenzene	0.7180	0.7184 [17]
		0.7150 [18]
		0.7134 [15]
o-Dichlorobenzene	1.1927	–

2.2. Methods

The binary mixtures were prepared by weight using a Mettler balance to a mole fraction accuracy of ± 0.0001 units. The viscometer was placed vertically in an electronically controlled thermostat which maintained at the temperature to a precision of $\pm 0.01°C$. The absolute viscosities of pure solvents and mixtures were evaluated using the relationship

$$\eta/(mPa\,s) = \rho/(g\,cm^{-3}) \quad \{At(s) - B/t(s)\} \tag{1}$$

where t = flow time, ρ = density, and A and B are the calibration constants estimated by measuring the flow times of double-distilled benzene and triple-distilled water and by solving the simultaneous equations derived for each. The flow times were measured with a stop watch capable of recording to 0.01 s. The viscosities were accurate to ± 0.0005 mPa s units.

3. Results and discussion

3.1. Correlation of experimental viscosities

The experimental viscosities and deviations from linear behavior for the acrylic ester–organic solvent mixtures at 303.15 K are listed in Table 2. An attempt was also made to correlate the experimental viscosities of the binary mixtures with different equations often employed for the prediction of viscosities of mixtures using adjustable parameters.

Grunberg and Nissan [19] gave the following relationship to express the viscosity of mixtures.

$$\ln \eta_{12} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \tag{2}$$

Table 2
Viscosities, η, and viscosity deviations, $\delta\eta$, of acrylic ester–organic solvent mixtures at 303.15 K

MMA–n-Hexane

x	η/mPa s	δη/mPa s
0.0731	0.2928	−0.0082
0.1732	0.3100	−0.0156
0.2754	0.3313	−0.0200
0.3520	0.3464	−0.0232
0.4652	0.3723	−0.0252
0.5482	0.3928	−0.0251
0.6519	0.4421	−0.0227
0.7277	0.4538	−0.0200
0.8399	0.4698	−0.0160
0.9177	0.4973	−0.0115
0.9791	0.5223	−0.0017

MMA–n-Heptane

x	η/mPa s	δη/mPa s
0.0240	0.3740	−0.0008
0.1404	0.3872	−0.0060
0.2282	0.3797	−0.0101
0.3569	0.4135	−0.0139
0.4738	0.4303	−0.0156
0.5583	0.4437	−0.0156
0.6194	0.4539	−0.0150
0.7088	0.4695	−0.0136
0.8160	0.4891	−0.0109
0.9094	0.5081	−0.0067
0.9991	0.5273	−0.0017

MMA–Carbon tetrachloride

x	η/mPa s	δη/mPa s
0.0320	0.8349	0.00001
0.0898	0.8160	−0.0006
0.1842	0.7843	−0.0025
0.2779	0.7537	−0.0035
0.3837	0.7184	−0.0054
0.4783	0.6885	−0.0054
0.5900	0.6523	−0.0063
0.6834	0.6232	−0.0059
0.7814	0.5929	−0.0053
0.8889	0.5610	−0.0032
0.9508	0.5432	−0.0014

MMA–Chlorobenzene

x	η/mPa s	δη/mPa s
0.0420	0.7035	−0.0066
0.1051	0.6844	−0.0137
0.2049	0.6606	−0.0187
0.3078	0.6397	−0.0202
0.4086	0.6202	−0.0206
0.5093	0.6033	−0.0185
0.6099	0.5871	−0.0157
0.7062	0.5726	−0.0120
0.8044	0.5570	−0.0090
0.9058	0.5439	−0.0030
0.9646	0.5353	−0.0005

MMA–o-Dichlorobenzene

x	η/mPa s	δη/mPa s
0.0456	1.1539	−0.0085
0.1114	1.1048	−0.0142
0.2108	1.0334	−0.0193
0.3166	0.9620	−0.0206
0.4149	0.8968	−0.0205
0.5164	0.8304	−0.0196
0.6158	0.7650	−0.0190
0.7159	0.7008	−0.0168
0.8092	0.6427	−0.0130
0.9032	0.5854	−0.0090
0.9643	0.5478	−0.0050

EMA–n-Hexane

x	η/mPa s	δη/mPa s
0.0396	0.2910	−0.0028
0.2079	0.3142	−0.0256
0.4065	0.3587	−0.0354
0.5102	0.3867	−0.0357
0.7082	0.4432	−0.0336
0.8027	0.4770	−0.0254
0.9640	0.5389	−0.0057

EMA–n-Heptane

x	η/mPa s	δη/mPa s
0.0489	0.3781	−0.0020
0.2294	0.4018	−0.0117
0.4379	0.4340	−0.0181
0.5397	0.4300	−0.0164
0.7290	0.4546	−0.0148
0.8248	0.4915	−0.0102
0.9635	0.5136	−0.0027

EMA–Carbon tetrachloride

x	η/mPa s	δη/mPa s
0.0343	0.8320	−0.0031
0.1638	0.7800	−0.0177
0.3394	0.7181	−0.0289
0.4350	0.6901	−0.0293
0.6448	0.6312	−0.0276
0.7620	0.6064	−0.0186
0.9444	0.5660	−0.0063

EMA–Chlorobenzene

x	η/mPa s	δη/mPa s
0.0358	0.7054	−0.0068
0.1699	0.6800	−0.0105
0.3526	0.6505	−0.0105
0.4478	0.6354	−0.0102
0.6550	0.6035	−0.0086
0.7647	0.5885	−0.0059
0.9487	0.5651	−0.0005

EMA–o-Dichlorobenzene

x	η/mPa s	δη/mPa s
0.0383	1.1704	0.0020
0.1842	1.0633	−0.0122
0.3691	0.9405	−0.0170
0.4699	0.8753	−0.0184
0.6734	0.7459	−0.0182
0.7787	0.6813	−0.0158
0.9555	0.5786	−0.0060

BMA–n-Hexane

x	η/mPa s	δη/mPa s
0.0331	0.2920	−0.0097
0.1715	0.3284	−0.0519
0.3526	0.3959	−0.0871
0.4450	0.4454	−0.0900
0.6553	0.5664	−0.0871
0.7626	0.6371	−0.0784
0.9475	0.7743	−0.0430

BMA–n-Heptane

x	η/mPa s	δη/mPa s
0.0394	0.3804	0.0225
0.1884	0.4270	−0.0344
0.3823	0.4838	−0.0706
0.4762	0.5232	−0.0763
0.6795	0.6266	−0.0704
0.7871	0.6918	−0.0569
0.9512	0.7969	−0.0305

BMA–Chlorobenzene

x	η/mPa s	δη/mPa s
0.0267	0.7220	−0.0005
0.1386	0.7474	−0.0111
0.2979	0.7770	0.0195
0.3879	0.7979	0.0284
0.5969	0.8321	0.0348
0.7182	0.8403	0.0269
0.9304	0.8483	0.0067

BMA–o-Dichlorobenzene

x	η/mPa s	δη/mPa s
0.0306	1.1916	0.0094
0.1518	1.1342	−0.0066
0.3186	1.0624	−0.0214
0.4145	1.0259	−0.0251
0.6200	0.9564	−0.0243
0.7358	0.9199	−0.0212
0.9408	0.8596	−0.0114

Heric [20] correlated the viscosity of mixtures with the relationships

$$\ln \eta_{12} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 \ln M_1 + x_2 \ln M_2 + \ln (x_1 M_1 + x_2 M_2) + H_{12} \quad (3)$$

McAllister [21] gave a two-parameter equation of the following type,

$$\ln \eta_{12} = x_1{}^3 \ln \eta_1 + 3x_1{}^2 x_2 (\ln M_{12}) + 3x_1 x_2{}^2 (\ln M_{21}) + x_2{}^3 \ln \eta_2$$
$$+ 3x_1{}^2 x_2 \ln ((2M_1 + M_2)/M_1) + 3x_2 x_1{}^2 \ln((2M_2 + M_1)/M_1)$$
$$+ 3x_1 x_2{}^2 \ln ((3M_1 + 2M_2)/3M_1) - \ln(x_1 + (x_2 M_2)/M_1) \quad (4)$$

Auslaender [22] correlated the mixture viscosity using the following equation containing three adjustable parameters,

$$x_1(x_1 + B_{12} x_2)(\eta_{12} - \eta_1) + A_{21} x_2 (B_{21} x_1 + x_2)(\eta_{12} - \eta_2) = 0 \quad (5)$$

The various parameters, viz. G_{12}, H_{12}, M_{12}, M_{21}, B_{12}, A_{21} and B_{21} that appear in Eqs. (2)–(5) are the adjustable parameters that must be determined by fitting the equations to the observed experimental viscosities; x, M, and η are the mole fraction, molecular weight and viscosities of the pure components (subscripts) 1 and 2 and the mixture (subscript 12).

The various adjustable parameters were evaluated from the fits of the experimental viscosity data to Eqs. (2)–(5) over the entire mole fraction range by a non-linear regression method on a computer program based on the Marquardt algorithm. The values of the parameters for all 14 binary mixtures containing an acrylic ester and an organic solvent, and the standard deviation, $\sigma(\%)$, are tabulated in Table 3. The $\sigma(\%)$ values were calculated from the relationship

$$\sigma(\%)/(\mathrm{mPa\,s}) = \left[\frac{1}{n-k} \left\{ \frac{100(\eta_{\mathrm{exp}} - \eta_{\mathrm{corr}})}{\eta_{\mathrm{exp}}} \right\}^2 \right]^{1/2} \quad (6)$$

where η_{exp} and η_{corr} are the experimental and correlated viscosities using Eqs. (2)–(5) and the adjustable parameters from Table 3. It can be seen from the table that the values of $\sigma(\%)$ for different correlating equations for all the binary mixtures studied were small and close to each other and the correlated viscosities were observed to be within the range of experimental precision. Thus it can be stated that the experimental viscosities of binary mixtures of acrylic esters and organic solvents may be equally well represented by all the correlating equations.

3.2. Viscosity deviations

The viscosity deviations as given in Table 2 for all the binary mixtures were calculated from the relationship

$$\delta \eta/(\mathrm{mPa\,s}) = \eta_{12} - (x_1 \eta_1 + x_2 \eta_2) \quad (7)$$

The $\delta \eta$ values were fitted through an equation of the type

$$\delta \eta/(\mathrm{mPa\,s}) = x(1-x) \sum_{i=0}^{i=n} a_i (2x-1)^i \quad (8)$$

Table 3
Adjustable parameters for Eqs. (2)–(5) and standard deviation, σ (%) of viscosities correlation of acrylic ester–organic solvent mixtures at 303.15 K

	Eq. (2)		Eq. (3)		Eq. (4)			Eq. (5)			
	G_{12}	σ	H_{12}	σ	M_{12}	M_{21}	σ	A_{21}	B_{21}	B_{12}	σ
MMA											
n-Hexane	−0.0270	0.024	0.0043	0.033	0.4543	0.3749	0.040	0.4116	3.1541	0.1911	0.040
n-Heptane	−0.0786	0.012	0.0127	0.008	0.4602	0.4026	0.009	0.4395	4.0132	0.3549	0.208
Carbon tetrachloride	0.0739	0.022	0.0169	1.000	0.6357	0.7529	0.066	0.1715	5.2667	0.1680	0.0002
Chlorobenzene	0.1986	1.510	−0.0248	0.263	0.5791	0.6159	0.720	0.1379	5.2399	0.3358	0
n-Dichlorobenzene	0.1694	0.104	−0.0386	0.020	0.8110	0.5839	3.410	0.2413	4.0466	0.3256	0.157
EMA											
n-Hexane	−0.1248	0.090	0.0528	0.434	0.3618	0.3477	0.525	0.2856	8.7296	0.2422	1.168
n-Heptane	−0.0719	0.046	−0.2069	0.162	0.4763	0.4140	0.070	0.1958	8.2970	0.1708	0.143
Carbon tetrachloride	−0.0876	0.008	0.0066	0.006	0.6238	0.7175	0.043	0.4525	1.0583	0.5880	0.201
Chlorobenzene	−0.188	0.391	0.0031	0.141	0.9502	0.6244	0.120	0.1469	7.5568	0.3901	0.878
o-Dichlorobenzene	0.1930	0.001	−0.0354	1.017	0.8237	0.9009	1.532	0.2068	3.4233	0.1742	0.249
BMA											
n-Hexane	−0.1785	0.147	0.0122	0.046	0.5933	0.3661	0.246	0.5190	4.8012	0.2496	0.478
n-Heptane	−2.1075	0.346	0.3235	0.089	0.6174	0.4602	0.026	0.4440	3.8717	0.2337	0.301
Chlorobenzene	0.1658	0.032	−0.0295	0.017	1.0132	0.7746	0.235	0.0839	4.0139	0.0778	0.016
o-Dichlorobenzene	−0.0424	0.060	0.0064	0.004	0.9217	1.0694	3.706	1.0507	−3.5339	0.0637	1.195

where x is the mole fraction of the ester molecules and a_i is the polynomial coefficient. The values of the coefficients a_i were evaluated by multiple regression analysis based on a least square method. The estimated coefficients and the standard deviations are given in Table 4.

The experimentally calculated $\delta\eta$ values together with the fitted values as calculated using Eq. (8) and the coefficients from Table 4 are shown as a function of ester mole fraction in Figs. 1–3. The viscosity deviations were, in general, found to be negative for all the mixtures containing MMA and EMA. However the $\delta\eta$ values were observed to be positive initially for BMA–n-heptane and BMA–dichlorobenzene mixtures. Furthermore $\delta\eta_{0.5}$ values were found to increase with the slight increase in the alkyl chain length of the aliphatic hydrocarbons, viz. n-hexane and n-heptane, in all mixtures. In contrast, for a given mixture containing aliphatic hydrocarbon, the $\delta\eta$ values were found to become more negative with increasing alkyl chain length of the methacrylic esters. Similarly, $\delta\eta$ values observed in EMA–carbon tetrachloride mixtures were more negative than those of MMA–carbon tetrachloride mixtures. We could not measure changes in the viscosities of BMA–carbon tetrachloride mixtures because the closeness of the viscosities of the individual components resulted in very small changes upon mixing. The trend in $\delta\eta_{0.5}$ values of the acrylic ester–chlorobenzene mixtures was found to be an increasing type, with even positive values for BMA–chlorobenzene mixtures. The $\delta\eta_{0.5}$ values for all three binary mixtures with MMA, EMA and BMA were found to be close in sign and magnitude.

Table 4

Least square coefficients of Eq. (8) for the representation of viscosity deviations of acrylic ester–organic solvent mixtures at 303.15 K

|	a_0	a_1	a_2	σ
MMA				
n-Hexane	− 0.101947	0.0004390	− 0.017744	0
n-Heptane	− 0.053670	− 0.042543	− 0.045783	0
Carbon tetrachloride	−0.024797	− 0.013751	0.007940	0.0001
Chlorobenzene	− 0.072200	0.079470	− 0.356400	0
o-Dichlorobenzene	− 0.073600	0.028410	− 0.099800	0.030
EMA				
n-Hexane	− 0.156271	− 0.036026	0.037337	0.0001
n-Heptane	− 0.071359	− 0.015203	0.014871	0
Carbon tetrachloride	− 0.122782	− 0.001818	0.016597	0.0001
Chlorobenzene	− 0.031364	0.072516	− 0.078401	0.00001
o-Dichlorobenzene	− 0.085172	− 0.071768	0.039641	0
BMA				
n-Hexane	− 0.350823	− 0.233826	− 0.273340	0.0001
n-Heptane	− 0.348417	− 0.467606	0.345666	0
Chlorobenzene	0.126088	0.086310	− 0.127384	0
o-Dichlorobenzene	− 0.137489	− 0.179187	0.195788	0
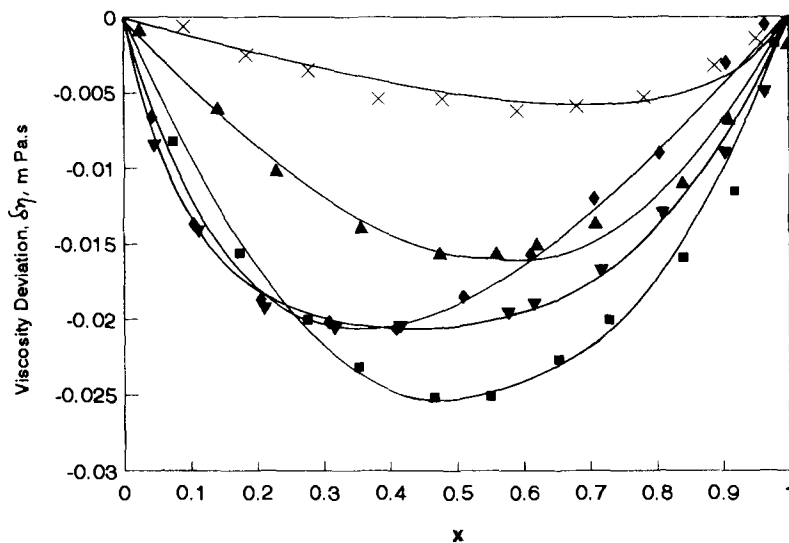
Fig. 1. Viscosity deviation of methyl methacrylate–organic solvent mixtures at 303.15 K: ■, n-hexane; ▲, n-heptane; x, carbon tetrachloride; ◆, chlorobenzene; ▼, o-dichlorobenzene ————— calculated from Eq. (8) and the coefficients from Table 4.
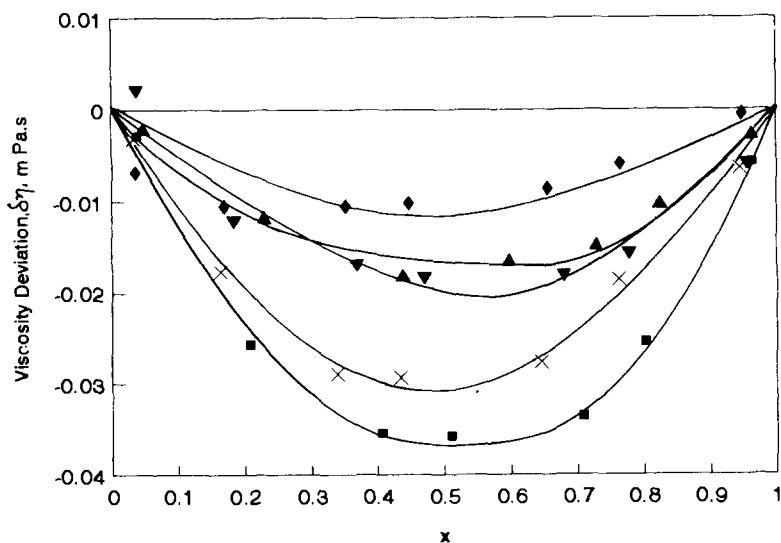

Fig. 2. Viscosity deviation of ethyl methacrylate–organic solvent mixtures at 303.15 K. Symbols as for Fig. 1.

The more negative or smaller $\delta\eta$ values indicated the presence of dispersing interactions and less negative and positive $\delta\eta$ values can be attributed to the balance of dispersing and specific interactions in the favour of the later. Thus the results presented in Table 2 and their trend in Figs. 1–3 indicate the presence of complex interactions.
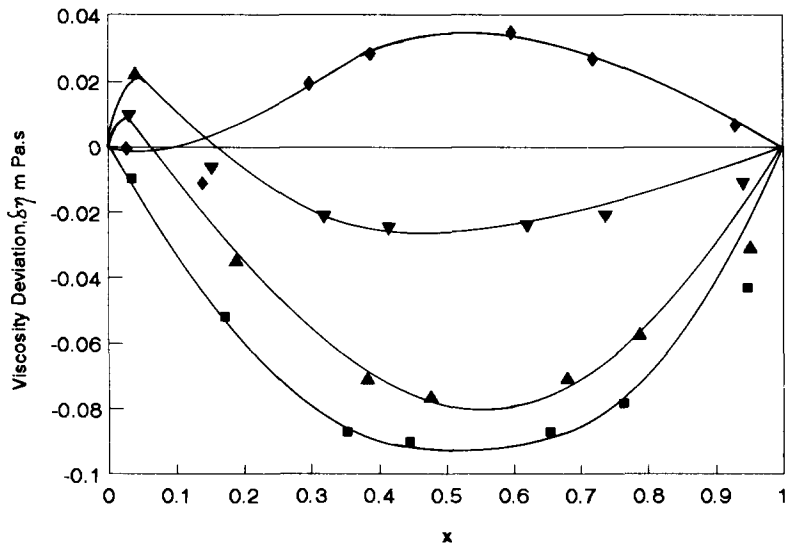
Fig. 3. Viscosity deviation butyl methacrylate–organic solvent mixtures at 303.15 K. Symbols as for Fig. 1.

3.3. Theoretical analysis

It was thought worthwhile to apply the Bloomfield–Dewan [23] approach based on Flory's free-volume theory to the viscosities of MMA–organic solvent mixtures to gain insight into the dominant thermodynamic factor that decides the mixtures viscosity. The thermodynamic contributions, viz. enthalpy, entropy and free volume, to the mixture viscosities i.e. $\ln \eta_H$, $\ln \eta_S$ and $\ln \eta_V$ were calculated for the binary MMA–organic solvent mixtures at an ester mole fraction of 0.5 by means of the relationships

$$\ln \eta_H = -\frac{\Delta H_m}{RT}$$

$$\ln \eta_S = \frac{\Delta S^R}{R} \quad \text{and}$$

$$\ln \eta_V = \frac{1}{\tilde{v} - 1} - \frac{x_1}{\tilde{v}_1 - 1} - \frac{x_2}{\tilde{v}_2 - 1}$$

The individual enthalpy and entropy contributions can be obtained from relationships proposed by Flory and coworkers [24,25] as given below,

$$\frac{\Delta H_m}{RT} = \frac{x_1 C_1}{\tilde{T}_1}\left(\frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}}\right) + \frac{x_2 C_2}{\tilde{T}_2}\left(\frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}}\right) + \frac{x_1 C_1 \theta_2 \chi_{12}}{\tilde{v}\,\tilde{T}_1 P_1{}^*} \tag{9}$$

Table 5
Enthalpic, entropic, free volume viscosities and their combinations for MMA–organic solvent mixtures at equimolar composition and 303.15 K

	η_H	η_V	η_S	η_{id}	$\eta_{id}\eta_H$	$\eta_{id}\eta_V$	$\eta_{id}\eta_S$	$\eta_{id}\eta_H\eta_V$	$\eta_{id}\eta_V\eta_S$	$\eta_{id}\eta_S\eta_H$	$\eta_{id}\eta_H\eta_V\eta_S$	η_{exp}
n-Hexane	0.7060	0.9232	1.1017	0.3870	0.2732	0.3573	0.4264	0.2522	0.3936	0.3010	0.2779	0.3836
n-Heptane	0.7535	0.9289	1.1018	0.4431	0.3339	0.4116	0.4882	0.3101	0.4535	0.3679	0.3417	0.4356
Carbon tetrachloride	0.8186	0.9419	1.0572	0.6686	0.5473	0.6298	0.7068	0.5153	0.6658	0.5786	0.5450	0.6812
Chlorobenzene	0.9528	0.9470	0.9939	0.6164	0.5873	0.5837	0.6126	0.5562	0.5802	0.5837	0.5528	0.5593
o-Dichlorobenzene	1.8539	0.6173	0.7430	0.7944	1.4727	0.4904	0.5902	0.9091	0.3644	1.0942	0.6755	0.8910

and

$$\frac{\Delta S^R}{R} = -3\left[\left\{x_1 C_1 \ln\,(\tilde{v}_1^{\,1/3} - 1)(\tilde{v}^{1/3} - 1)^{-1}\right\}\right.$$
$$\left. + \left\{x_2 C_2 \ln(\tilde{v}_2^{\,1/3} - 1)(\tilde{v}^{1/3} - 1)^{-1}\right\}\right] \tag{10}$$

The various terms that appear in Eqs. (9) and (10) are derived by following the Flory formalism. The reduced volumes of the mixture and the pure components, v_i and v are calculated by use of experimental densities and thermal expansion coefficients. The parameter C_i for a given pure component is defined as,

$$C_i = P_i^* \, V_i^* (RT_i^*)^{-1} \tag{11}$$

The characteristic parameters needed in the above calculations and the interaction parameter χ_{12} estimated from a fit of experimental equimolar excess volume data were reported in our earlier paper [14].

The individual values of η_H, η_V and η_S at an equimolar fraction of MMA and their combinations together with the ideal viscosities, η_{id}, for the various binary mixtures are presented in Table 5. It is found that the combination $\eta_{id}\eta_V\eta_S$ is close to the experimental viscosities in MMA–n-hexane and MMA–n-heptane mixtures. This indicates that both the free volume changes upon mixing, unlike the molecular and entropy changes due to the dispersing interactions, are dominant in MMA–aliphatic hydrocarbon mixtures. Similarly both $\eta_{id}\eta_S$ and $\eta_{id}\eta_V\eta_S$ were observed to be close to the experimental viscosities for MMA–carbon tetrachloride mixtures, whereas for MMA–chlorobenzene mixtures, where specific interactions between the ester and Cl groupings through O–Cl linkages, are expected to be present in addition to the dispersing interactions, the experimental viscosities were best represented by combinations of $\eta_{id}\eta_H$ and $\eta_{id}\eta_V$. However it is interesting to note that the experimental viscosities of MMA–o-dichlorobenzene mixtures was best expressed by the combined product $\eta_{id}\eta_H\eta_V$ whereas the individual $\eta_{id}\eta_H$ and $\eta_{id}\eta_V$ were found to be either too high or too low in comparison with the experimental viscosities. This it can be envisaged that the bulky Cl groups in the 1,2 position of o-dichlorobenzene weaken the specific interactions in these mixtures.

Acknowledgements

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