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Thermodynamics of Acrylic Ester–Organic Solvent Mixtures. V. Viscosities and Excess Viscosities of Alkyl Acrylates–1-Alcohol Binary Mixtures at 298.15 and 308.15 K

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The viscosities for 12 binary mixtures of methyl acrylate (MA), ethyl acrylate (EA), and butyl acrylate (BA)-1-heptanol, -1-octanol, -1-decanol, and -1-dodecanol were measured at 298.15 and 308.15 K. The excess viscosities were calculated from the results. The typical variations in the viscosities and excess viscosities of the mixtures as a function of ester mole fractions were explained in terms of structure-breaking dispersion and ester–ester-like interactions. The viscosities can be reasonably correlated in terms of Grunberg-Nissan, McAllister, and Auslander equations.

KEY WORDS: acrylic esters; 1-alcohols, viscosity; excess viscosity.

1. INTRODUCTION

Acrylic esters are important industrial chemicals and are used primarily as precursors in the production of technically important specialty polymers. The production of acrylic esters from lower to higher alkyl homologues is done by either direct esterification with the corresponding alcohol or trans-esterification reaction in an inert solvent medium. Thus the measurements involving the changes in the various physical properties upon mixing acrylic esters with alcohols or alkanes and all three components together provide valuable information for the optimization of various process parameters for the efficient design of reactors for the transesterification

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process. In addition, the derived excess properties and their dependence on the composition of ester species help in understanding the molecular interactions between the binary acrylic ester–alcohol or acrylic ester–alkane and ternary acrylic ester–alcohol–alkane mixtures.

A literature survey of thermodynamic studies involving liquid mixtures containing acrylic esters as one of the components revealed that only a few measurements on excess enthalpies and volumes have been reported for methyl methacrylate–ethanol or –propanol [1] and methyl methacrylate–alkanes [2–4]. Data on the viscosity of liquid mixtures containing either acrylic esters or aliphatic esters as one of the components are scarce. This prompted us to embark on a research program involving extensive measurements of volumetric, transport, acoustic, and dielectric properties of binary, as well as of ternary mixtures, involving combinations of acrylic ester, alcohol, and aliphatic or aromatic hydrocarbons. In previous papers the densities, speeds of sound, excess volumes, and isentropic compressibilities [5–7], viscosity functions [8, 9], and dielectric functions [10] involving binary mixtures of alkyl methacrylates (methyl, ethyl, or butyl)–1-alcohols or –alkanes have been reported. The results presented in this paper are part of our effort to create an extensive database for various physical properties of the above mixtures and use them for understanding the complex molecular interactions and also for developing the group contribution parameters for a quantitative prediction of such properties. The dynamic viscosities of the methyl, ethyl, and butyl acrylate–1-heptanol, –1-octanol, –1-decanol, and –1-dodecanol were measured at 298.15 and 308.15 K. The excess viscosities were computed from the data. An attempt is also made to give a qualitative interpretation of the dependence of the excess viscosity on the alkyl chain length of both components.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

Methyl acrylate was obtained from Aldrich, while ethyl acrylate and butyl acrylate of purum grade were obtained from Fluka. The purity of these chemicals is stated to be more than 99% on a mole basis and they were used as such without any further treatment. The acrylic esters were, however, stabilized with about 0.002% hydroquinone monomethyl ether. The 1-alcohols were the same as used in our earlier work [11]. A comparison of our measured densities and viscosities of the pure components with the literature values as presented in Table I shows a good agreement of our data with the literature values.

Table I. Literature Comparison of Densities (ρ) and Viscosities (η) of Pure Components at 298.15 and 308.15 K

	ρ (g·cm^{-3})				η (mPa·s)			
	298.15 K		308.15 K		298.15 K		308.15 K	
	This work	Lit.	This work	Lit.	This work	Lit.	This work	Lit.
1-Heptanol	0.8189	0.81942 [12]	0.8126	0.81228 [12]	5.7700	5.7740 [14]	4.2663	4.2630 [14]
1-Octanol	0.8212	0.8216 [13]	0.8146	0.8146 [13]	7.3630	7.3630 [14]	5.2500	5.2560 [14]
1-Decanol	0.8265	0.8263 [13]	0.8195	0.8194 [13]	11.7900	11.7980 [16]	8.1241	7.5690 [15]
1-Dodecanol	0.8281	0.82995 [12]	0.8217	0.8232 [12]	16.1355	—	11.3153	11.6330 [15]
Methyl acrylate	0.9475	—	0.9356	—	0.4492	—	0.3909	—
Ethyl acrylate	0.9163	—	0.9046	—	0.5177	—	0.4559	—
Butyl acrylate	0.8941	—	0.8846	—	0.7868	—	0.6843	—

2.2. Methods

The binary mixtures were prepared in stoppered glass vials on a mass basis with an estimated mole fraction precision of ±0.0001 U. The mixing of the components was done in hermetically scaled glass vials to prevent any evaporation losses during solution preparation.

Dynamic viscosities, η, were measured with Ubbelhode-type viscometers. The viscometers were calibrated with triple-distilled water and cyclohexane for estimating the calibration constants A and B at both temperatures by solving simultaneous equations of the form

$$\eta = \rho[At - (B/t)] \tag{1}$$

where η is the dynamic viscosity in mPa · s, ρ is the density in $g \cdot cm^{-3}$ and t is the flow time in s. The densities of the pure components as well as those of the mixtures were determined with the aid of a precalibrated bicapillary pyknometer. The flow times were measured with a stopwatch capable of registering the time with a precision of ±0.1 s. The measured densities and viscosities are accurate to ±0.0001 and ±0.001 U, respectively. The following density and viscosity data for triple-distilled water ($\rho_{25} = 0.9970$, $\rho_{35} = 0.9940$ $g \cdot cm^{-3}$; $\eta_{25} = 0.8937$, $\eta_{35} = 0.7225$) and cyclohexane ($\rho_{25} = 0.7737$, $\rho_{35} = 0.7640$ $g \cdot cm^{-3}$; $\eta_{25} = 0.8876$, $\eta_{35} = 0.7546$ mPa · s) were employed. The pyknometer and viscometer were placed vertically in a thermostated water bath maintained at the measuring temperature with an overall precision of ±0.01°C.

3. RESULTS AND DISCUSSION

The experimental data for the densities and viscosities at 298.15 and 308.15 K for all the binary mixtures are presented in Tables II and III, respectively. The dependence of the mixture viscosities on the ester mole fraction is also shown graphically in Fig. 1. It is interesting to note from the figure that there are three distinct regions in all the curves. In the first region, the viscosities were observed to decrease sharply (up to $x_1 \approx 0.3$), followed by a continuous decrease (second region). The third region is characterized by very close values (above $x_1 \approx 0.8$). Large variations in the viscosities were observed for a given ester with the increase in the carbon-chain length of alcohols from 1-heptanol to 1-dodecanol in the initial ester mole fraction range. The mixture viscosities in the higher ester mole fraction range were, however, found to be very close to each other and they were almost independent of the chain length of the 1-alcohols for a given ester.

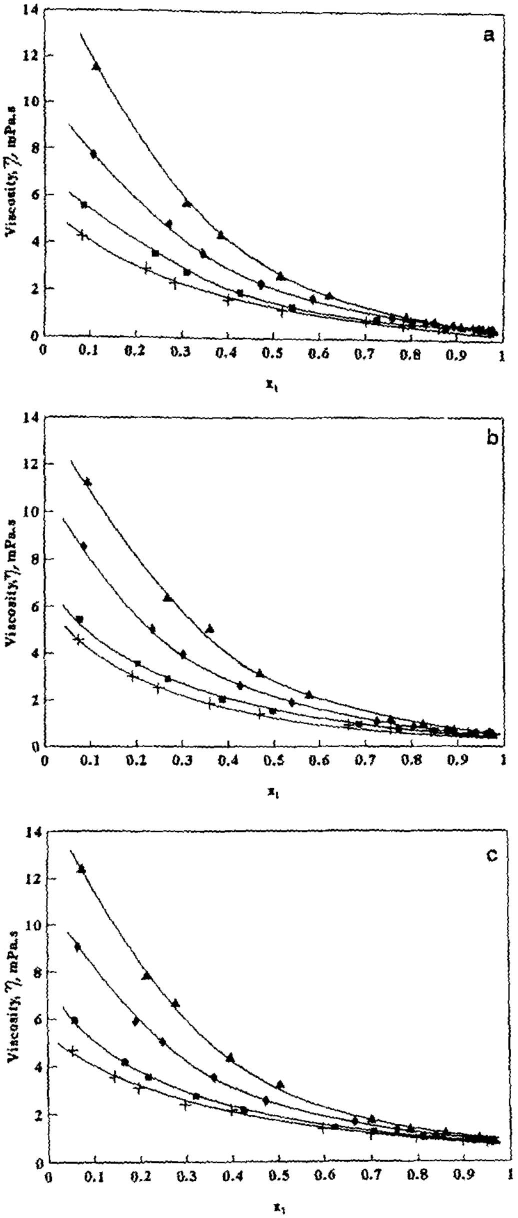

Fig. 1. Dependence of the viscosity of the binary mixtures on the acrylic ester mole fraction at 298.15 K: (a) methyl acrylate–, (b) ethyl acrylate–, and (c) butyl acrylate–(+) 1-heptanol, (■) 1-octanol, (◆) 1-decanol, and (▲) 1-dodecanol.

Table II. Densities (ρ) and Viscosities (η_{mix}) of the Ester + 1-Alcohols at 298.15 K[a]

x_1	ρ ($g \cdot cm^{-3}$)	η_{mix} (mPa · s)	x_1	ρ ($g \cdot cm^{-3}$)	η_{mix} (mPa · s)	x_1	ρ ($g \cdot cm^{-3}$)	η_{mix} (mPa · s)	x_1	ρ ($g \cdot cm^{-3}$)	η_{mix} (mPa · s)
MA (1) + 1-heptanol (2)			MA (1) + 1-octanol (2)			MA (1) + 1-decanol (2)			MA (1) + 1-dodecanol (2)		
0.0803	0.8252	4.278	0.0847	0.8268	5.555	0.1056	0.8318	7.732	0.1127	0.8325	11.572
0.2190	0.8366	2.912	0.2398	0.8383	3.533	0.2709	0.8421	4.826	0.3078	0.8436	5.722
0.2841	0.8424	2.304	0.3089	0.8441	2.795	0.3442	0.8476	3.593	0.3842	0.8492	4.400
0.4009	0.8540	1.632	0.4269	0.8553	1.948	0.4717	0.8588	2.331	0.5147	0.8603	2.703
0.5184	0.8674	1.218	0.5391	0.8677	1.353	0.5843	0.8707	1.712	0.6206	0.8715	1.891
0.7017	0.8927	0.783	0.7233	0.8930	0.857	0.7574	0.8946	0.938	0.7884	0.8953	0.992
0.7824	0.9058	0.653	0.8011	0.9060	0.692	0.8309	0.9076	0.738	0.8506	0.9071	0.785
0.8604	0.9197	0.563	0.8748	0.9198	0.566	0.8923	0.9202	0.639	0.9093	0.9205	0.629
0.9347	0.9340	0.493	0.9408	0.9337	0.506	0.9483	0.9334	0.519	0.9554	0.9331	0.530
0.9686	0.9409	0.467	0.9698	0.9403	0.470	0.9749	0.9404	0.482	0.9794	0.9406	0.484
EA (1) + 1-heptanol (2)			EA (1) + 1-octanol (2)			EA (1) + 1-decanol (2)			EA (1) + 1-dodecanol (2)		
0.0736	0.8240	4.585	0.0771	0.8257	5.444	0.0861	0.8302	8.526	0.0932	0.8314	11.284
0.1906	0.8326	3.017	0.2017	0.8337	3.576	0.2350	0.8381	5.017	0.2669	0.8396	6.404
0.2456	0.8368	2.513	0.2664	0.8383	2.914	0.3020	0.8421	3.969	0.3351	0.8435	5.497

0.3599	0.8460	1.864	0.3869	0.8475	2.043	0.4261	0.8505	2.618	0.4687	0.8521	3.183
0.4687	0.8556	1.399	0.4933	0.8566	1.543	0.5383	0.8593	1.895	0.5769	0.8603	2.253
0.6637	0.8752	0.923	0.6865	0.8756	0.960	0.7248	0.8770	1.076	0.7542	0.8773	1.192
0.7551	0.8854	0.778	0.7722	0.8852	0.785	0.8036	0.8861	0.860	0.8231	0.8857	0.963
0.8399	0.8956	0.655	0.8504	0.8949	0.681	0.8763	0.8959	0.702	0.8907	0.8956	0.740
0.9223	0.9060	0.576	0.9275	0.9054	0.582	0.9389	0.9055	0.602	0.9643	0.9087	0.584
0.9662	0.9118	0.534	0.9634	0.9107	0.546	0.9688	0.9106	0.563	0.9743	0.9108	0.565
BA (1) + 1-heptanol (2)			BA (1) + 1-octanol (2)			BA (1) + 1-decanol (2)			BA (1) + 1-dodecanol (2)		
0.0538	0.8228	4.656	0.0586	0.8248	5.944	0.0646	0.8295	9.073	0.0750	0.8308	12.418
0.1451	0.8295	3.548	0.1668	0.8318	4.170	0.1907	0.8358	5.873	0.2149	0.8369	7.842
0.1979	0.8334	3.084	0.2181	0.8352	3.544	0.2493	0.8390	4.998	0.2782	0.8399	6.982
0.2976	0.8408	2.394	0.3218	0.8421	2.729	0.3612	0.8454	3.536	0.3968	0.8461	4.373
0.3981	0.8482	2.166	0.4238	0.8492	2.165	0.4732	0.8522	2.535	0.5042	0.8523	3.244
0.5964	0.8628	1.350	0.6226	0.8634	1.403	0.6650	0.8651	1.653	0.7015	0.8655	1.769
0.6984	9.8703	1.120	0.7052	0.8696	1.232	0.7560	0.8719	1.303	0.7849	0.8721	1.376
0.7966	0.8778	0.981	0.8125	0.8780	0.998	0.8402	0.8788	1.070	0.8614	0.8789	1.197
0.8968	0.8856	0.869	0.9095	0.8860	0.900	0.9227	0.8862	0.905	0.9327	0.8862	0.983
0.9498	0.8900	0.824	0.9529	0.8898	0.850	0.9615	0.8901	0.843	0.9651	0.8899	0.858

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[a] MA, methyl acrylate; EA, ethyl acrylate; BA, Butyl acrylate.

Table III. Densities (ρ) and Viscosities (η) of the Ester + 1-Alcohols at 308.15 K^a

x_1	ρ ($g \cdot cm^{-3}$)	η_{mix} ($mPa \cdot s$)	x_1	ρ ($g \cdot cm^{-3}$)	η_{mix} ($mPa \cdot s$)	x_1	ρ ($g \cdot cm^{-3}$)	η_{mix} ($mPa \cdot s$)	x_1	ρ ($g \cdot cm^{-3}$)	η_{mix} ($mPa \cdot s$)
MA (1) + 1-heptanol (2)			MA (1) + 1-octanol (2)			MA (1) + 1-decanol (2)			MA (1) + 1-dodecanol (2)		
0.0803	0.8186	3.262	0.0847	0.8200	4.155	0.1056	0.8246	5.659	0.1127	0.8260	8.309
0.2190	0.8299	2.282	0.2398	0.8314	2.757	0.2709	0.8348	3.531	0.3078	0.8305	4.391
0.2841	0.8356	1.857	0.3089	0.8371	2.060	0.3442	0.8400	2.828	0.3842	0.8426	3.385
0.4009	0.8468	1.348	0.4269	0.8477	1.583	0.4717	0.8504	1.792	0.5147	0.8521	2.157
0.5184	0.8595	1.032	0.5391	0.8595	1.127	0.5843	0.8617	1.425	0.6206	0.8628	1.515
0.7017	0.8834	0.677	0.7233	0.8837	0.732	0.7574	0.8849	0.804	0.7884	0.8866	0.833
0.7824	0.8960	0.568	0.8011	0.8963	0.622	0.8309	0.8977	0.641	0.8506	0.8984	0.668
0.8604	0.9083	0.490	0.8748	0.9097	0.497	0.8923	0.9101	0.540	0.9093	0.9115	0.549
0.9347	0.9230	0.428	0.9408	0.9229	0.433	0.9483	0.9227	0.459	0.9554	0.9231	0.473
0.9686	0.9295	0.411	0.9698	0.9290	0.415	0.9749	0.9292	0.432	0.9794	0.9297	0.438
EA (1) + 1-heptanol (2)			EA (1) + 1-octanol (2)			EA (1) + 1-decanol (2)			EA (1) + 1-dodecanol (2)		
0.0736	0.8175	3.306	0.0771	0.8190	4.096	0.0861	0.8232	6.006	0.0932	0.8248	10.083
0.1906	0.8258	2.411	0.2017	0.8267	2.812	0.2350	0.8309	3.812	0.2669	0.8325	4.772
0.2456	0.8298	2.010	0.2664	0.8310	2.301	0.3020	0.8347	3.085	0.3351	0.8362	4.182

0.3599	0.8387	1.531	0.3869	0.8396	1.663	0.4261	0.8426	2.104	0.4687	0.8444	2.515
0.4687	0.8478	1.180	0.4933	0.8482	1.268	0.5383	0.8508	1.515	0.5769	0.8522	1.748
0.6637	0.8660	0.778	0.6865	0.8663	0.825	0.7248	0.8677	0.898	0.7542	0.8683	0.997
0.7551	0.8755	0.658	0.7722	0.8756	0.678	0.8036	0.8764	0.730	0.8231	0.8763	0.792
0.8399	0.8849	0.564	0.8504	0.8848	0.586	0.8763	0.8856	0.060	0.8907	0.8855	0.633
0.9223	0.8947	0.505	0.9275	0.8946	0.507	0.9389	0.8946	0.525	0.9643	0.8977	0.512
0.9662	0.9002	0.471	0.9634	0.8995	0.478	0.9688	0.8993	0.497	0.9743	0.8995	0.497
BA (1) + 1-heptanol (2)			BA (1) + 1-octanol (2)			BA (1) + 1-decanol (2)			BA (1) + 1-dodecanol (2)		
0.0538	0.8165	3.481	0.0586	0.8182	4.393	0.0646	0.8224	6.488	0.0750	0.8244	8.748
0.1451	0.8230	2.761	0.1668	0.8249	3.177	0.1907	0.8285	4.404	0.2149	0.8302	5.789
0.1979	0.8267	2.398	0.2181	0.8281	2.752	0.2493	0.8316	3.679	0.2782	0.8331	4.807
0.2976	0.8337	1.922	0.3218	0.8347	2.096	0.3612	0.8378	2.762	0.3968	0.8392	3.380
0.3981	0.8407	1.719	0.4238	0.8414	1.689	0.4732	0.8444	2.073	0.5042	0.8450	2.459
0.5964	0.8547	1.084	0.6226	0.8552	1.146	0.6650	0.8569	1.301	0.7015	0.8576	1.409
0.6984	0.8620	0.925	0.7052	0.8613	0.992	0.7560	0.8635	1.115	0.7849	0.8639	1.135
0.7966	0.8692	0.836	0.8125	0.8694	0.841	0.8402	0.8702	0.897	0.8614	0.8704	1.004
0.8968	0.8767	0.736	0.9095	0.8771	0.753	0.9227	0.8773	0.781	0.9327	0.8773	0.860
0.9498	0.8807	0.705	0.9529	0.8807	0.715	0.9615	0.8809	0.723	0.9651	0.8806	0.732

[a] MA, methyl acrylate; EA, ethyl acrylate; BA, Butyl acrylate.

Table IV. Excess Viscosities (η^E) of the Ester + 1-Alcohols at 298.15 and 308.15 K^a

	η^E (mPa · s)			η^E (mPa · s)			η^E (mPa · s)			η^E (mPa · s)	
	298.15 K	308.15 K		298.15 K	308.15 K		298.15 K	308.15 K		298.15 K	308.15 K
MA (1) + 1-heptanol (2)			MA (1) + 1-octanol (2)			MA (1) + 1-decanol (2)			MA (1) + 1-dodecanol (2)		
0.0803	−1.065	−0.693	0.0847	−1.222	−0.683	0.1056	−2.859	−1.649	0.1127	−2.796	−1.649
0.2190	−1.693	−1.136	0.2398	−2.172	−1.328	0.2709	−3.892	−2.498	0.3078	−5.585	−2.498
0.2841	−1.955	−1.309	0.3089	−2.432	−1.689	0.3442	−4.293	−2.634	0.3842	−5.708	−2.634
0.4009	−2.005	−1.365	0.4269	−2.464	−1.593	0.4717	−4.109	−2.684	0.5147	−5.508	−2.684
0.5184	−1.794	−1.225	0.5391	−2.283	−1.504	0.5843	−3.452	−2.181	0.6206	−5.358	−2.181
0.7017	−1.253	−0.870	0.7233	−1.505	−1.003	0.7574	−2.262	−1.463	0.7884	−4.510	−1.463
0.7824	−0.954	−0.666	0.8011	−1.133	−0.736	0.8309	−1.629	−1.057	0.8506	−2.776	−1.057
0.8604	−0.629	−0.442	0.8748	−0.749	−0.502	0.8923	−1.036	−0.684	0.9093	−2.008	−0.684
0.9347	−0.304	−0.216	0.9408	−0.353	−0.245	0.9483	−0.516	−0.332	0.9554	−1.243	−0.332
0.9686	−0.149	−0.101	0.9698	−0.188	−0.122	0.9749	−0.252	−0.154	0.9794	−0.289	−0.154
EA (1) + 1-heptanol (2)			EA (1) + 1-octanol (2)			EA (1) + 1-decanol (2)			EA (1) + 1-dodecanol (2)		
0.0736	−0.799	−0.680	0.0771	−1.391	−0.784	0.0861	−2.293	−1.458	0.0932	−3.396	−2.396
0.1906	−1.752	−1.129	0.2017	−2.407	−1.471	0.2350	−4.124	−2.501	0.2669	−5.563	−3.645

0.2456	−1.968	−1.320	0.2664	−2.626	−1.672	0.3020	−4.417	−2.723	0.3351	−5.705	−3.887
0.3599	−2.018	−1.364	0.3869	−2.671	−1.732	0.4261	−4.369	−2.753	0.4687	−5.633	−3.711
0.4687	−1.909	−1.300	0.4933	−2.443	−1.617	0.5383	−3.827	−2.481	0.5769	−4.872	−3.303
0.6637	−1.361	−0.960	0.6865	−1.704	−1.134	0.7248	−2.544	−1.666	0.7542	−3.165	−2.128
0.7551	−1.026	−0.731	0.7722	−1.292	−0.870	0.8036	−1.872	−1.232	0.8231	−2.317	−1.585
0.8399	−0.704	−0.502	0.8504	−0.861	−0.587	0.8763	−1.210	−0.798	0.8907	−1.485	−1.010
0.9223	−0.350	−0.247	0.9275	−0.432	−0.297	0.9389	−0.604	−0.400	0.9643	−0.491	−0.331
0.9662	−0.158	−0.113	0.9634	−0.199	−0.138	0.9688	−0.306	−0.198	0.9743	−0.354	−0.238
BA (1) + 1-heptanol (2)			BA (1) + 1-octanol (2)			BA (1) + 1-decanol (2)			BA (1) + 1-dodecanol (2)		
0.0538	−0.846	−0.592	0.0586	−1.034	−0.590	0.0646	−2.006	−1.156	0.0750	−2.566	−1.770
0.1451	−1.499	−0.985	0.1668	−2.096	−1.312	0.1907	−3.820	−2.307	0.2149	−4.995	−3.241
0.1979	−1.700	−1.160	0.2181	−2.385	−1.502	0.2493	−4.049	−2.590	0.2782	−4.884	−3.551
0.2976	−1.893	−1.278	0.3218	−2.518	−1.685	0.3612	−4.279	−2.675	0.3968	−5.672	−3.717
0.3981	−1.920	−1.291	0.4238	−2.511	−1.626	0.4732	−4.049	−2.531	0.5042	−5.153	−3.496
0.5964	−1.448	−1.046	0.6226	−1.865	−1.262	0.6650	−2.820	−1.875	0.7015	−3.600	−2.449
0.6984	−1.170	−0.840	0.7052	−1.494	−1.038	0.7560	−2.168	−1.385	0.7849	−2.713	−1.836
0.7966	−0.819	−0.577	0.8125	−1.022	−0.700	0.8402	−1.475	−0.976	0.8614	−1.718	−1.154
0.8968	−0.433	−0.318	0.9095	−0.482	−0.344	0.9227	−0.732	−0.478	0.9327	−0.837	−0.540
0.9498	−0.213	−0.159	0.9529	−0.246	−0.184	0.9615	−0.367	−0.248	0.9651	−0.465	−0.323

[a] MA, methyl acrylate; EA, ethyl acrylate; BA, Butyl acrylate.

The observed large dilution of the 1-alcohol viscosities in the initial additions of the acrylic esters suggests the dominance of structure-breaking dispersion interactions. However, at high ester mole fractions ester–ester-like interactions seem to be more predominant over ester -1–alcohol dispersion interactions as indicated by the lower viscosities as described above. To gain further insight into these interesting changes in the mixture viscosities, the excess viscosities, η^E were evaluated as

$$\eta^E = \eta_{\text{mix}} - (x_1\eta_1 + x_2\eta_2) \tag{2}$$

where η_{mix} is the mixture viscosity, and x_i and η_i are the mole fractions and viscosities of ester (1) and 1-alcohol (2) components, respectively. The η^E data at 298.15 and 308.15 K for all the mixtures are presented in Table IV. The excess viscosities are also represented mathematically by an equation of the form

$$\eta^E = x_1(1 - x_1) \sum_{i=0}^{2} a_i(2x_1 - 1)^i \tag{3}$$

where x_1 is the ester mole fraction and a_i a coefficient. The values of the coefficients, a_i, were estimated by a multiple regression analysis based on the method of least squares and are summarized in Table V along with the standard deviations σ.

A graphical comparison of the dependence of η^E on the ester mole fraction for methyl, ethyl, and butyl acrylate–1-alcohols is shown in Fig. 2. It can be seen that the η^E values for all the mixtures were negative over the entire ester mole fraction range. A steep decrease in the excess viscosities was noted in the initial ester mole fractions. The decrease in the ester-rich regions was gradual, however, the curves were skewed toward ester mole fractions of about $x_1 \approx 0.3$–0.4. The latter range is denoted the second region in Fig. 1. A further striking feature in Fig. 2 is that the η^E value for a given 1-alcohol was found to show very little variation with the ester alkyl chain length from methyl to butyl acrylate. The η^E values were found to become more negative with an increase in the carbon-chain length of 1-alcohol for any given ester mixture. Large negative values were noted for ester–1-dodecanol mixtures at both temperatures. A comparison of our previously measured η^E data at 303.15 K for methyl methacrylate–1-alcohol (methanol to 1-hexanol) mixtures [8] reveals that the magnitude of the present η^E values for MA–higher 1-alcohols is more negative than that of similar data for lower 1-alcohols. A rise in temperature was found to reduce the magnitude of η^E in all mixtures. However, the trend in the $\eta^E - \text{vs} - x_1$ curves appears to be same at 298.15 and 308.15 K.

Table V. Coefficients, a_i, and Standard Deviation, σ, for Representation of the Excess Viscosities of Ester + 1-Alcohols at 298.15 and 308.15 K

	298.15 K				308.15 K			
	a_0	a_1	a_2	σ	a_0	a_1	a_2	σ
MA +								
1-Heptanol	−7.1537	5.0418	−3.1425	0.002	−4.9237	3.1662	1.8477	0.002
1-Octanol	−9.2349	5.2184	−2.4744	0.002	−6.2044	2.6680	−0.5492	0.002
1-Decanol	−15.3842	11.3541	−7.0676	0.002	−9.9650	6.2464	−3.0839	0.002
1-Dodecanol	−22.2701	10.3430	−1.7785	0.002	−14.7942	6.2549	−0.2459	0.001
EA +								
1-Heptanol	−7.5624	4.37566	−1.3851	0.001	−4.9353	3.4336	−2.1825	0.001
1-Octanol	−9.6494	7.3467	−4.0859	0.001	−6.4389	3.8669	−1.5778	0.001
1-Decanol	−15.9742	10.6561	−5.3041	0.001	−10.2540	6.5117	−3.2563	0.001
1-Dodecanol	−21.3541	14.6507	−8.2470	0.001	−14.2118	10.3640	−6.4914	0.001
BA +								
1-Heptanol	−6.4973	5.9573	−4.6403	0.001	−4.4330	3.7120	−3.2841	0.001
1-Octanol	−9.1286	6.9272	−3.7273	0.003	−6.1887	3.7138	−1.6037	0.001
1-Decanol	−15.0664	12.0935	−8.0038	0.001	−9.7053	6.6885	−4.0185	0.001
1-Dodecanol	−20.3336	12.6673	−6.3382	9.001	−13.7169	8.7673	−4.5284	0.001

The observed large negative η^E values in general indicate a high dilution of 1-alcohol viscosities in the presence of the ester species as already noted in Fig. 1. The decrease in viscosity values can be ascribed to the breaking-up of 1-alcohol associates by unlike ester molecules. This type of interaction seems to be dominant when the share of ester in the mixture is small. In the ester-rich mixtures dispersion interactions are expected to be replaced by ester–ester-like interactions as indicated by the closeness of the viscosity values in Fig. 1 and by the gradual decrease in the η^E values in Fig. 2 in this range.

3.1. Correlation of Mixture Viscosities

The estimation of mixture viscosities by semiempirical approaches is of great industrial utility. The viscosities of binary liquid mixtures are often represented by equations of the form

$$\ln \eta_{\mathrm{mix}} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \tag{4}$$

$$\begin{aligned}\ln \eta_{\mathrm{mix}} = {} & x_1^3 \ln \eta_1 + 3x_1^2 x_2 (\ln M_{12}) + 3x_1 x_2^2 (\ln M_{21}) \\ & + x_2^3 \ln \eta_2 + 3x_1^2 x_2 \ln((\tfrac{2}{3} + M_3/3M_1) + 3x_1 x_2^2 \ln((\tfrac{1}{3} + 2M_2/3M_1) \\ & + x_2^3 \ln(M_2/M_1) - \ln(x_1 + (x_2 M_2)/M_1)\end{aligned} \tag{5}$$

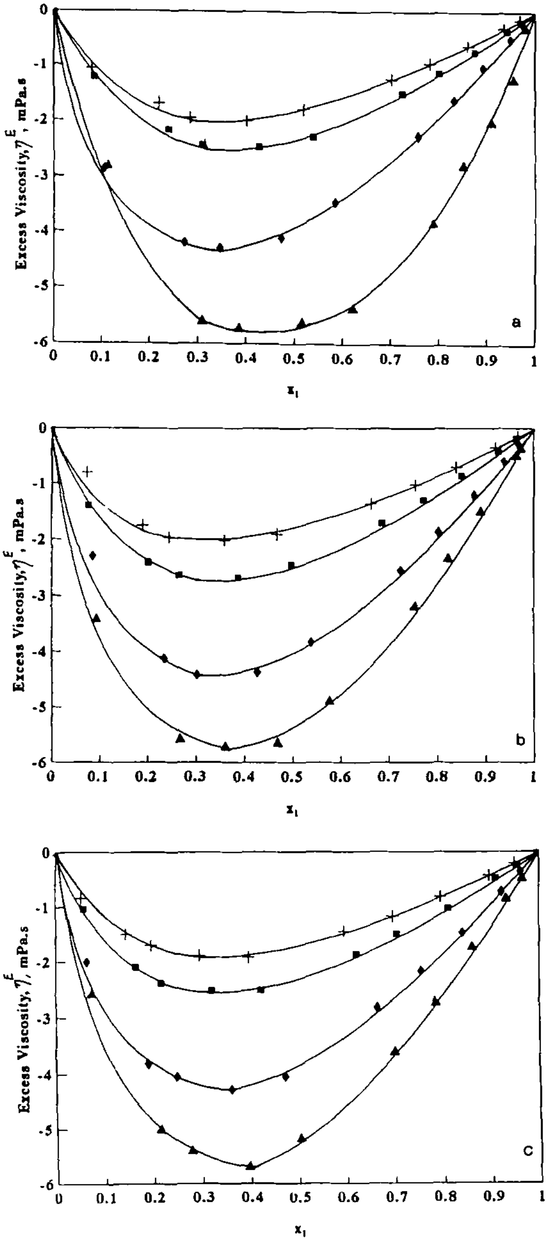

Fig. 2. Excess viscosity as a function of ester mole fraction at 298.15 K. Symbols the same as in Fig. 1.

Table VI. Adjustable Parameters in Eqs. (4) (6) for Representation of Mixture Viscosities at 298.15 and 308.15 K

	MA + 1-heptanol	MA + 1-octanol	MA + 1-decanol	MA + 1-dodecanol	EA + 1-heptanol	EA + 1-octanol	EA + 1-decanol	EA + 1-dodecanol	BA + 1-heptanol	BA + 1-octanol	BA + 1-decanol	BA + 1-dodecanol
298.15 K												
G_{12}	−0.9671	−0.6227	−0.2384	−0.1071	−1.1263	−1.0635	−0.6631	−0.0399	−1.1621	−1.1795	−0.9508	0.3295
σ	0.004	0.003	0.010	0.2	0.002	0.008	0.001	0.10	0.030	0.001	0.007	0.004
M_{12}	0.7718	0.8854	1.2749	1.6294	0.8303	0.9163	1.0500	1.6641	1.1169	0.5894	0.7010	0.8371
M_{21}	1.7105	2.4702	3.6914	5.7916	1.7385	2.0631	3.8080	5.3854	1.8793	3.0259	4.7465	8.1858
σ	0.002	0.003	0.001	0.002	0.002	0.001	0.003	0.003	0.002	0.001	0.002	0.001
A_{21}	2.9096	0.6979	4.5098	0.0096	0.0269	0.2912	0.1548	2.0199	0.0901	0.0762	0.5333	0.3364
B_{21}	−0.0401	0.0409	−0.0336	8.8915	5.9343	0.3594	0.7043	−0.0352	2.7126	2.2051	0.1755	0.5495
B_{12}	12.7809	2.5834	20.9106	−0.0611	0.0656	1.3148	0.6196	8.7044	0.4684	0.3209	2.4927	1.2725
σ	0.002	0.003	0.001	0.001	0.003	0.001	0.001	0.002	0.001	0.001	0.001	0.001
308.15 K												
G_{12}	−0.7734	−0.4487	−0.0901	0.1849	−0.9925	−0.8631	−0.5207	0.0842	−1.1209	−1.1320	−0.8217	−0.4224
σ	0.004	0.003	0.006	0.010	0.003	0.004	0.002	0.001	0.006	0.003	0.002	0.004
M_{12}	0.7032	0.8371	1.1152	1.3745	0.6945	0.7669	0.9243	1.1965	0.8868	0.2954	0.4533	0.4142
M_{21}	1.3656	1.8069	2.7896	4.3710	1.4490	1.7684	2.4724	4.7908	1.5624	3.0615	8.5626	7.3934
σ	0.002	0.001	0.002	0.002	0.002	0.001	0.001	0.002	0.001	0.002	0.001	0.002
A_{21}	3.9669	0.3047	1.3341	0.0113	3.1468	0.1922	0.6867	0.0401	0.0107	0.1150	0.3011	1.0766
B_{21}	−0.0266	0.3767	0.0400	8.7948	−0.0209	0.7338	0.0900	2.8958	23.2956	1.3105	0.4836	0.0543
B_{12}	15.6752	0.8975	5.1806	−0.0553	13.1917	0.6900	2.7073	−0.0349	0.0660	0.3996	1.2017	4.1580
σ	0.003	0.002	0.001	0.002	0.001	0.002	0.001	0.003	0.001	0.001	0.001	0.002

and

$$x_1(x_1 + B_{12}x_2)(\eta_{\text{mix}} - \eta_1) + A_{21}x_2(B_{21}x_1 + x_2)(\eta_{\text{mix}} - \eta_2) = 0 \qquad (6)$$

Equations (4)–(6) are known as Grunberg–Nissan, McAllister, and Auslander equations, respectively; the x_i terms are the mole fractions, η_{mix} is the mixture viscosity, and η_i is the viscosity of pure ester (1) and of 1-alcohol (2). The terms G_{12}, M_{12}, M_{21}, A_{21}, B_{21}, and B_{12} are adjustable parameters representing the binary interactions and were determined by experimental fits of the viscosities through a nonlinear regression analysis using Marquardt algorithm. The values of the parameters along with the standard deviations, σ, between the experimental and the correlated viscosities are given in Table VI. The estimated smaller σ values indicate that the present mixture viscosities can be correlated by all three equations equally well.

4. CONCLUSIONS

Structure-breaking dispersion interactions are dominant in the initial ester mole fraction range for acrylic ester–1-alcohol binary mixtures. However, the forces between like molecules seem to be more pronounced than between unlike molecules in the ester-rich regions. The balance of these two forces is expected to be dominant in the intermediate mole fraction range. The acrylic ester–1-alcohol mixture viscosities can be reasonably well represented by the Grunberg–Nissan, McAllister, and Auslander equations.

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