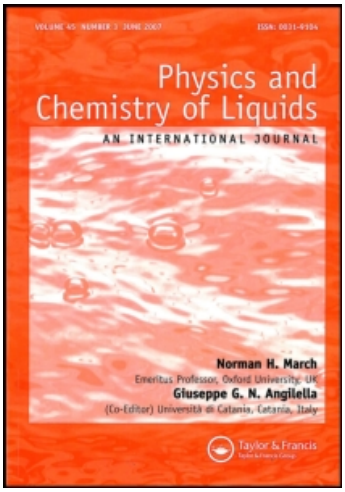

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Volumetric Behaviour of Acrylic Esters (Methyl-, Ethyl-, and Butyl Acrylate) 1-Alcohol (Heptanol, Octanol, Decanol and Dodecanol) at 298.15 K and 308.15 K

N. V. Sastry[a]; M. K. Valand[a]
[a] Department of Chemistry, Sardar Patel University, Vidyanagar, Gujarat, India

To cite this Article Sastry, N. V. and Valand, M. K.(2000) 'Volumetric Behaviour of Acrylic Esters (Methyl-, Ethyl-, and Butyl Acrylate) 1-Alcohol (Heptanol, Octanol, Decanol and Dodecanol) at 298.15 K and 308.15 K', Physics and Chemistry of Liquids, 38: 1, 61 — 72
To link to this Article: DOI: 10.1080/00319100008045297
URL: http://dx.doi.org/10.1080/00319100008045297

Phys. Chem. Liq., 2000, Vol. 38, pp. 61–72
Reprints available directly from the publisher
Photocopying permitted by license only

VOLUMETRIC BEHAVIOUR OF ACRYLIC ESTERS (METHYL-, ETHYL-, AND BUTYL ACRYLATE) + 1-ALCOHOL (HEPTANOL, OCTANOL, DECANOL AND DODECANOL) AT 298.15 K AND 308.15 K

N. V. SASTRY* and M. K. VALAND

Department of Chemistry, Sardar Patel University,
Vallabh Vidyanagar-388 120, Gujarat, India

(Received 3 September 1998)

New experimental data on densities and excess volumes (V^E) for methyl acrylate (MA) +, ethyl acrylate (EA) +, or butyl acrylate (BA) + 1-heptanol, + 1-octanol, + 1-decanol and + 1-dodecanol are reported at (298.15 and 308.15) K. The excess volumes were fitted to Redlisch-Kister type equation. The variations in excess volumes with the alkyl chain length of both the components are explained in terms of molecular interactions.

Keywords: Densities; excess volumes; alkyl acrylate-1-alcohol mixtures

1. INTRODUCTION

The mixing of an alcohol with other molecules often results into the dissociation of the former and the specific interactions between the dissociated alcohol species with the second component molecules, when the later are polar and non specific interactions when they are non polar can thus be expected. Such structure breaking and making interactions can be considered as chief factors that contribute to the sign and magnitude of the thermodynamic excess properties of this kind of mixtures. Acrylate esters of higher homologues are produced

* Corresponding author.

by either direct esterification or by an ester interchange reactions between the lower acrylates and higher alcohols. Hence the knowledge of thermodynamic properties of acrylate ester + alcohol binary mixtures is useful in optimising the process parameters and also aids in an efficient design of the transesterification process in the industrial scale. There exists relatively few thermodynamic studies in the literature dealing with the acrylic ester–organic solvent mixtures as compared to the large available data on aliphatic ester containing mixtures in spite of the greater industrial use of the former. In addition the availability of wide and systematic data base on the various thermo-physical properties of binary mixtures facilitates the development of group contribution methods for the theoretical prediction of mixture properties from the pure component data.

Keeping these interests in view, we have reported the excess molar volumes and isentropic compressibilities [1] and viscosity functions [2] for methyl methacrylate + 1-alcohol (up to 1-hexanol) mixtures at 303.15 K and 313.15 K. The present work is part of our comprehensive investigations on various thermodynamic, transport and dielectric properties of acrylate ester + alcohol, + alkane, alcohol + alkane binary mixtures and acrylic ester + alcohol + alkane ternary mixtures. The densities at 298.15 K and 308.15 K are measured for binary mixtures of acrylic esters namely methyl acrylate, or ethyl acrylate or butyl acrylate + 1-heptanol, + 1-octanol, + 1-decanol and + 1-dodecanol. The excess volumes of the mixtures are calculated and discussed in terms of the chain lengths of both the components.

2. EXPERIMENTAL

Methyl acrylate was Aldrich product, while ethyl acrylate and butyl acrylate were of Fluka purum grade chemicals. The purity of these chemicals is stated to be more than 99% on mole basis and were used as such without any further treatment. The acrylic esters were however stabilised with about 0.002% hydroquinone monomethyl ether. The 1-alcohols were the same as used in our earlier work [3]. The experimentally measured densities of all the pure components are given in Table I along with the available comparable literature values at both the measuring temperatures.

TABLE I Densities (ρ/g·cm^{-3}) of pure components at 298.15 K and 308.15 K

	298.15 K		308.15 K	
	This work	*Lit.*	*This work*	*Lit.*
1-Heptanol	0.8189	0.81942 [7]	0.8126	0.81228 [7]
1-Octanol	0.8212	0.8216 [8]	0.8146	0.8146 [8]
1-Decanol	0.8265	0.8263 [8]	0.8195	0.8194 [8]
1-Dodecanol	0.8281	0.82995 [7]	0.8217	0.8232 [7]
Methyl acrylate	0.9475	–	0.9356	–
Ethyl acrylate	0.9163	–	0.9046	–
Butyl acrylate	0.8941	–	0.8846	–

The binary mixtures were prepared in stoppered glass vials on a Mettler balance with an estimated mole fraction accuracy of ± 0.0001. The densities of the pure and mixture components were measured by a bicapillary pyknometer with an accuracy of ± 0.0001 units. The pyknometer was calibrated with triple distilled water. The temperature during the density measurements was controlled to an absolute precision of 0.01 °C.

3. RESULTS AND DISCUSSION

The experimental data of densities and excess volumes, V^E of all the acrylic ester + 1-alcohol mixtures are given in Tables II and III at 298.15 K and 308.15 K respectively. The V^E values were calculated from the relation,

$$V^E/\text{cm}^3\,\text{mol}^{-1} = \frac{x_1M_1 + x_2M_2}{\rho_{12}} - \left(\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}\right) \qquad (1)$$

where x and ρ are the mole fraction, density of pure ester (1), 1-alcohol (2) and mixture (12) components. M is the molecular weight of respective pure components. The experimental V^E data of the binary mixtures is further fitted by an equation of the form,

$$V^E/\text{cm}^3\,\text{mol}^{-1} = x_1(1 - x_1)\Sigma\, a_i(2x_1 - 1)^i \qquad (2)$$

The values of the coefficients a_i needed for the mathematical representation of V^E data for individual mixtures at both the temperatures were estimated by using a multiple regression analysis

TABLE II Densities (ρ) and excess volumes (V^E) for the ester + 1-alcohols at 298.15 K

x_1	ρ $g \cdot cm^{-3}$	V^E cm^3 mol^{-1}	x_1	ρ $g \cdot cm^{-3}$	V^E cm^3 mol^{-1}	x_1	ρ $g \cdot cm^{-3}$	V^E cm^3 mol^{-1}	x_1	ρ $g \cdot cm^{-3}$	V^E cm^3 mol^{-1}
MA (1) + 1-Heptanol (2)			MA (1) + 1-Octanol (2)			MA (1) + 1-Decanol (2)			MA (1) + 1-Dodecanol (2)		
0.0803	0.8248	0.152	0.0847	0.8268	0.140	0.1056	0.8318	0.243	0.1127	0.8328	0.284
0.2190	0.8364	0.324	0.2398	0.8383	0.379	0.2709	0.8424	0.435	0.3078	0.8442	0.452
0.2841	0.8424	0.387	0.3089	0.8441	0.464	0.3442	0.8480	0.485	0.3842	0.8497	0.496
0.4009	0.8543	0.451	0.4269	0.8552	0.573	0.4717	0.8592	0.554	0.5147	0.8607	0.580
0.5184	0.8676	0.502	0.5391	0.8675	0.620	0.5843	0.8710	0.595	0.6206	0.8716	0.650
0.7017	0.8922	0.474	0.7233	0.8925	0.545	0.7574	0.8943	0.571	0.7884	0.8949	0.649
0.7824	0.9049	0.412	0.8011	0.9055	0.440	0.8309	0.9670	0.497	0.8506	0.9066	0.576
0.8604	0.9185	0.320	0.8748	0.9193	0.320	0.8923	0.9196	0.370	0.9093	0.9201	0.420
0.9347	0.9331	0.177	0.9408	0.9334	0.163	0.9483	0.9330	0.209	0.9554	0.9328	0.242
0.9686	0.9404	0.089	0.9698	0.9401	0.088	0.9749	0.9402	0.106	0.9794	0.9404	0.118
EA (1) + 1-Heptanol (2)			EA (1) + 1-Octanol (2)			EA (1) + 1-Decanol (2)			EA (1) + 1-Dodecanol (2)		
0.0736	0.8248	0.087	0.0771	0.8259	0.089	0.0861	0.8306	0.107	0.0932	0.8318	0.127
0.1906	0.8326	0.204	0.2017	0.8340	0.232	0.2350	0.8386	0.265	0.2669	0.8401	0.289
0.2456	0.8368	0.260	0.2664	0.8386	0.283	0.3020	0.8426	0.332	0.3351	0.8439	0.340
0.3599	0.8461	0.343	0.3869	0.8477	0.382	0.4261	0.8509	0.427	0.4687	0.8522	0.471
0.4687	0.8557	0.385	0.4933	0.8567	0.420	0.5383	0.8595	0.492	0.5769	0.8603	0.540
0.6637	0.8752	0.336	0.6865	0.8755	0.412	0.7248	0.8771	0.499	0.7542	0.8771	0.593
0.7551	0.8854	0.269	0.7722	0.8852	0.353	0.8036	0.8863	0.434	0.8231	0.8856	0.533
0.8399	0.8955	0.188	0.8504	0.8944	0.268	0.8763	0.8960	0.332	0.8907	0.8956	0.396
0.9223	0.9059	0.098	0.9275	0.9054	0.151	0.9389	0.9056	0.190	0.9643	0.9087	0.169
0.9662	0.9117	0.044	0.9634	0.9146	0.079	0.9688	0.9107	0.098	0.9743	0.9108	0.118

BA (1) + 1-Heptanol (2)			BA (1) + 1-Octanol (2)			BA (1) + 1-Decanol (2)			BA (1) + 1-Dodecanol (2)		
0.0538	0.8228	0.032	0.0586	0.8248	0.054	0.0646	0.8295	0.073	0.0750	0.8309	0.066
0.1451	0.8295	0.070	0.1668	0.8318	0.107	0.1907	0.8359	0.160	0.2149	0.8367	0.171
0.1979	0.8334	0.086	0.2181	0.8352	0.126	0.2493	0.8390	0.205	0.2782	0.8396	0.217
0.2976	0.8407	0.125	0.3218	0.8422	0.161	0.3612	0.8454	0.248	0.3968	0.8455	0.303
0.3981	0.8481	0.155	0.4238	0.8492	0.199	0.4732	0.8522	0.293	0.5042	0.8514	0.376
0.5964	0.8628	0.188	0.6226	0.8300	0.242	0.6650	0.8651	0.333	0.7015	0.8648	0.443
0.6984	0.8704	0.194	0.7052	0.8696	0.246	0.7560	0.8719	0.326	0.7849	0.8716	0.411
0.7966	0.8778	0.184	0.8125	0.8780	0.212	0.8402	0.8788	0.276	0.8614	0.8787	0.330
0.8968	0.8856	0.115	0.9095	0.8860	0.142	0.9227	0.8863	0.168	0.9327	0.8862	0.195
0.9498	0.8900	0.058	0.9529	0.8898	0.084	0.9615	0.8901	0.093	0.9651	0.8899	0.110

MA = Methyl Acrylate, EA = Ethyl Acrylate, BA = Butyl Acrylate.

TABLE III Densities (ρ) and excess volumes (V^E) for the ester + 1-alcohols at 308.15 K

x_1	ρ $g \cdot cm^{-3}$	V^E cm^3 mol^{-1}	x_1	ρ $g \cdot cm^{-3}$	V^E cm^3 mol^{-1}	x_1	ρ $g \cdot cm^{-3}$	V^E cm^3 mol^{-1}	x_1	ρ $g \cdot cm^{-3}$	V^E cm^3 mol^{-1}
MA (1) + 1-Heptanol (2)			MA (1) + 1-Octanol (2)			MA (1) + 1-Decanol (2)			MA (1) + 1-Dodecanol (2)		
0.0803	0.8185	0.109	0.0847	0.8201	0.116	0.1056	0.8249	0.173	0.1127	0.8265	0.200
0.2190	0.8297	0.270	0.2398	0.8314	0.310	0.2709	0.8351	0.370	0.3078	0.8374	0.378
0.2841	0.8354	0.342	0.3089	0.8371	0.374	0.3442	0.8405	0.419	0.3842	0.8426	0.438.
0.4009	0.8466	0.428	0.4269	0.8479	0.465	0.4717	0.8511	0.521	0.5147	0.8510	0.548
0.5184	0.8595	0.466	0.5391	0.8597	0.514	0.5843	0.8625	0.554	0.6206	0.8634	0.620
0.7017	0.8831	0.433	0.7233	0.8836	0.462	0.7574	0.8849	0.530	0.7884	0.8858	0.606
0.7824	0.8953	0.366	0.8011	0.8958	0.393	0.8309	0.8972	0.444	0.8506	0.8970	0.524
0.8604	0.9084	0.265	0.8748	0.9089	0.288	0.8923	0.9091	0.341	0.9093	0.9098	0.381
0.9347	0.9222	0.140	0.9408	0.9222	0.154	0.9483	0.9220	0.177	0.9554	0.9218	0.218
0.9686	0.9291	0.061	0.9698	0.9286	0.080	0.9749	0.9286	0.096	0.9794	0.9290	0.101
EA (1) + 1-Heptanol (2)			EA (1) + 1-Octanol (2)			EA (1) + 1-Decanol (2)			EA (1) + 1-Dodecanol (2)		
0.0736	0.8176	0.057	0.0771	0.8191	0.080	0.0861	0.8234	0.104	0.0932	0.8251	0.147
0.1906	0.8258	0.163	0.2017	0.8269	0.199	0.2350	0.8311	0.238	0.2669	0.8331	0.260
0.2456	0.8298	0.214	0.2664	0.8313	0.244	0.3020	0.8350	0.283	0.3351	0.8368	0.284
0.3599	0.8386	0.297	0.3869	0.8401	0.313	0.4261	0.8430	0.356	0.4687	0.8449	0.357
0.4687	0.8478	0.321	0.4933	0.8486	0.338	0.5383	0.8513	0.399	0.5769	0.8526	0.417
0.6637	0.8661	0.295	0.6865	0.8669	0.321	0.7248	0.8681	0.397	0.7542	0.8686	0.451
0.7551	0.8757	0.235	0.7722	0.8757	0.280	0.8036	0.8768	0.341	0.8231	0.8765	0.413
0.8399	0.8857	0.160	0.8504	0.8848	0.209	0.8763	0.8859	0.256	0.8907	0.8857	0.313
0.9223	0.8950	0.072	0.9275	0.8946	0.111	0.9389	0.8948	0.145	0.9643	0.8977	0.135
0.9662	0.9004	0.028	0.9634	0.9033	0.059	0.9688	0.8994	0.085	0.9743	0.8996	0.095

BA (1) + 1-Heptanol (2)			BA (1) + 1-Octanol (2)			BA (1) + 1-Decanol (2)			BA (1) + 1-Dodecanol (2)		
0.0538	0.8164	0.021	0.0586	0.8181	0.046	0.0646	0.8224	0.071	0.0750	0.8245	0.080
0.1451	0.8228	0.064	0.1668	0.8249	0.086	0.1907	0.8286	0.151	0.2149	0.8303	0.192
0.1979	0.8265	0.087	0.2181	0.8281	0.118	0.2493	0.8316	0.192	0.2782	0.8332	0.228
0.2976	0.8336	0.108	0.3218	0.8348	0.158	0.3612	0.8378	0.228	0.3968	0.8391	0.281
0.3981	0.8407	0.135	0.4238	0.8416	0.182	0.4732	0.8444	0.264	0.5042	0.8451	0.302
0.5964	0.8548	0.163	0.6226	0.8223	0.189	0.6650	0.8570	0.272	0.7015	0.8579	0.307
0.6984	0.8622	0.148	0.7052	0.8614	0.191	0.7560	0.8637	0.239	0.7849	0.8643	0.267
0.7966	0.8693	0.134	0.8125	0.8695	0.152	0.8402	0.8704	0.181	0.8614	0.8708	0.206
0.8968	0.8766	0.092	0.9095	0.8771	0.096	0.9227	0.8775	0.097	0.9327	0.8775	0.123
0.9498	0.8807	0.054	0.9529	0.8807	0.046	0.9615	0.8810	0.050	0.9651	0.8808	0.072

MA = Methyl Acrylate, EA = Ethyl Acrylate, BA = Butyl Acrylate.

based on least square method. The values of the coefficients along with the estimated standard deviations, σ between the experimental and fitted values are presented in Table IV.

A graphical comparison of the V^E results at 298.15 and 308.15 K for the binary mixtures of each acrylic ester + 1-alcohols is given in Figures 1–3, where the excess volumes are plotted against the mole fraction of the ester species. It can be seen from the figure that the V^E values are positive for all the mixtures. The curves are skewed towards the ester rich regions ($x_1 > 0.6$). A systematic dependence of V^E values on the alkyl chain length of the 1-alcohols for a given set of ester + 1-alcohols was also noted. A careful examination of all the curves shows that the V^E values in the lower mole fraction region ($x_1 < 0.4$) were close to each other for all the four alcohols with any given ester, while large and appreciable variations in V^E values were noted in the mole fraction regions of $x_1 = 0.4-0.8$ and $x_1 > 0.8$ respectively.

However the magnitude of V^E values was found to show diminishing trend for a given 1-alcohol mixtures with the increase in the ester alkyl chain length from methyl acrylate to butyl acrylate. The excess volumes in general were decreased with the rise in the temperature for all the mixtures. The temperature coefficient $(\partial V^E/\partial T)_{0.5}$ was found to be

TABLE IV Coefficients, a_i and standard deviation, σ for the least square representation of excess volumes of ester + 1-alcohols at 298.15 K 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	1.9700	0.4599	0.6508	0.003	1.8991	0.4373	−0.1388	0.003
1-Octanol	2.4403	0.6686	−0.0983	0.002	2.0052	0.7011	0.1256	0.004
1-Decanol	2.2786	0.8285	1.4915	0.003	2.1225	1.0271	0.8552	0.002
1-Dodecanol	2.2791	1.3173	2.5935	0.002	2.1562	1.5599	1.6932	0.003
EA +								
1-Heptanol	1.5141	0.0626	−0.2828	0.004	1.3558	0.0956	−0.6160	0.003
1-Octanol	1.7088	0.5482	0.0442	0.003	1.3889	0.3102	0.0137	0.004
1-Decanol	1.9155	1.0809	0.4832	0.004	1.5375	0.7170	0.5678	0.004
1-Dodecanol	1.9533	1.6982	1.4093	0.002	1.4834	1.0236	1.5997	0.004
BA +								
1-Heptanol	0.7914	0.3953	0.2743	0.003	0.0610	0.3241	0.2230	0.003
1-Octanol	0.8418	0.5076	0.6914	0.002	0.7603	0.2076	0.2217	0.004
1-Decanol	1.2040	0.6917	0.7915	0.003	1.0827	0.1768	0.2074	0.005
1-Dodecanol	1.4939	1.2454	0.7115	0.004	1.2082	0.4441	0.5018	0.004

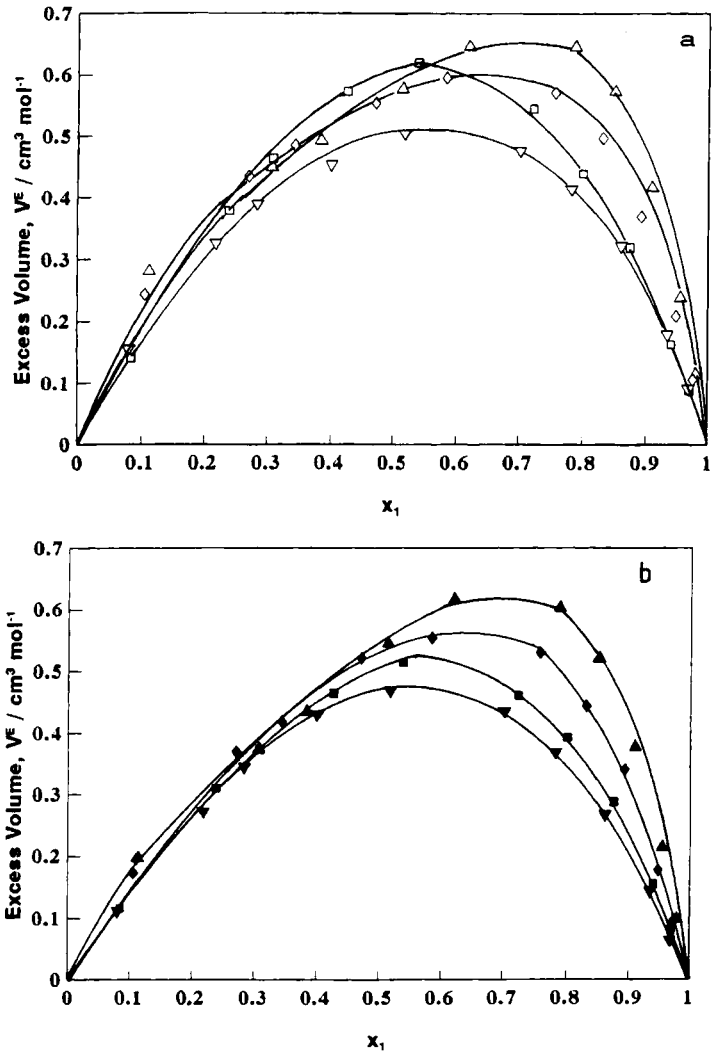

FIGURE 1 Excess volumes for methyl acrylate + 1-alcohols at (a) 298.15 K (open) and (b) 308.15 K (bold). (▽) 1-heptanol, (□) 1-octanol, (◇) 1-decanol, (△) 1-dodecanol.

negative with no systematic variations with the alkyl chain length of both the components.

To the best of our knowledge there is no literature data either on densities or excess volumes of same mixtures for a direct comparison

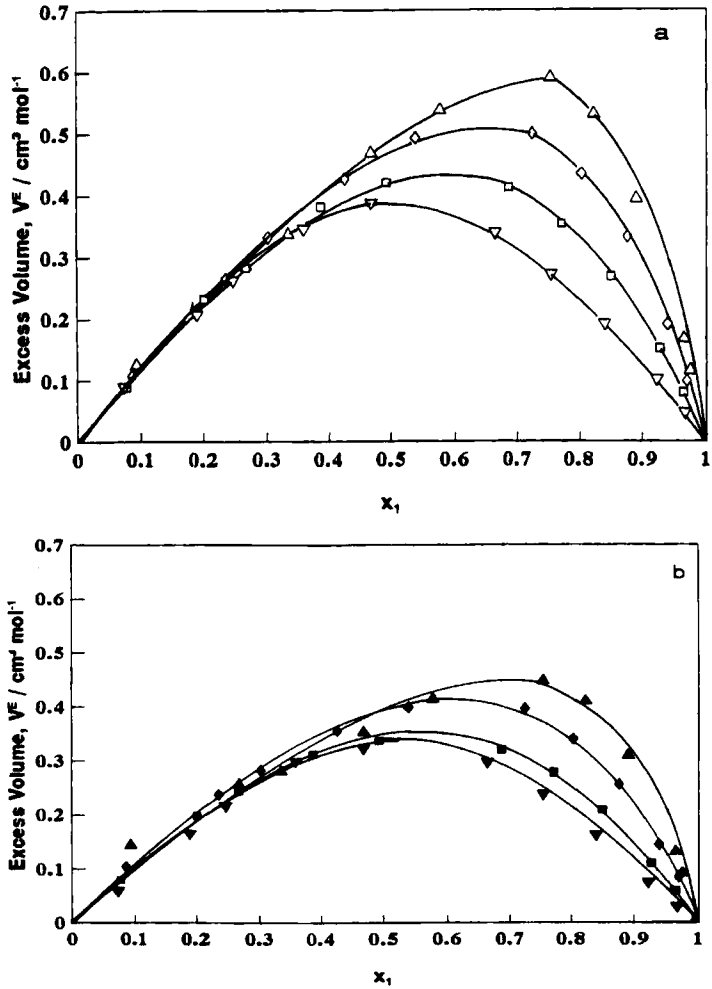

FIGURE 2 Excess volumes for ethyl acrylate + 1-alcohols at (a) 298.15 K (open) and (b) 308.15 K (bold). Legends same as Figure 1.

of our results. Even we are unable to find the literature V^E data for the same 1-alcohol mixtures with the methyl-, ethyl- or butyl propanoates, where the later have similar molecular structures as MA, EA and BA and the only difference being the presence of unsaturation in the acrylic esters, for an indirect comparison. Two types of interactions can be considered for the qualitative interpretations of excess volume

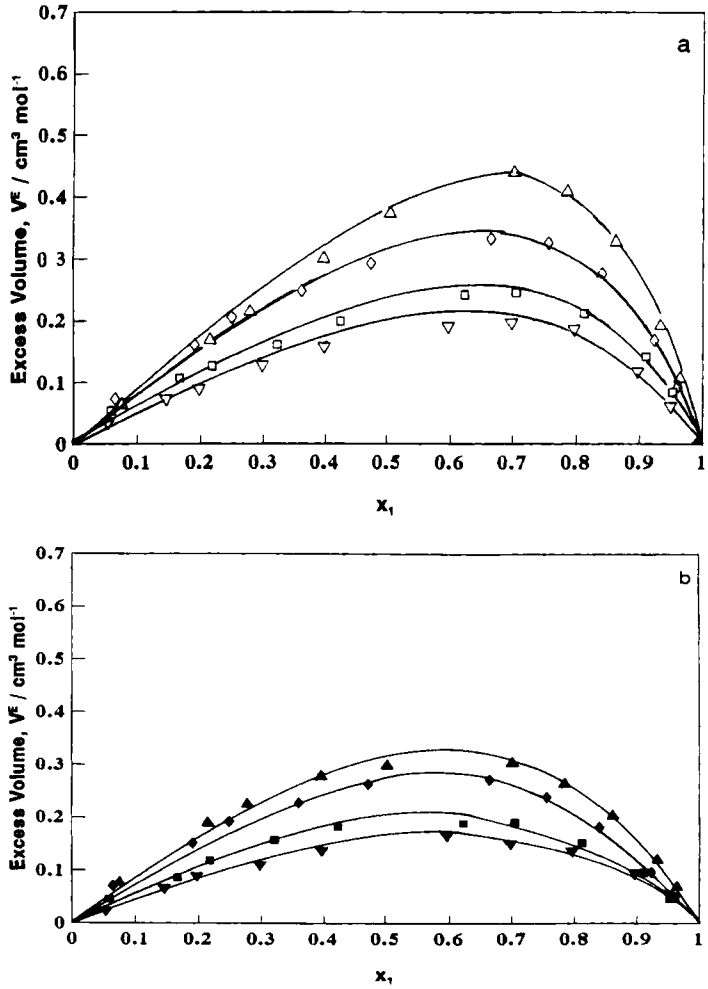

FIGURE 3 Excess volumes for butyl acrylate + 1-alcohols at (a) 298.15 K (open) and (b) 308.15 K (bold). Legends same as Figure 1.

data of ester–alcohol mixtures. The first type of interaction includes either the breaking of associate structures of 1-alcohol species by unlike ester species and also weakening of dipolar forces in the ester molecules in presence of added second polar component. The second category of interactions are of specific type in which the interstitial accommodation of ester into 1-alcohol associate structures can occur

and also the formation of new associates through ester–OH hydrogen bonding may take place. The first type of interactions may lead to positive V^E values and while negative V^E values are observed when specific interactions are dominant. Thus our observed positive excess volumes for the present mixtures and their systematic variations with the chain length of both the ester and 1-alcohol species suggest the dominance of non specific interactions. Our conclusions agree qualitatively with the interpretation of literature reported excess volumes of ethyl acetate + or propyl acetate + 1-alcohols (C_2 to C_{10}) [4], methyl alkanoates (acetate, propanoate and butanoate) + 1-alcohols (from ethanol to 1-pentanol) [5], *n*-alkyl esters (methyl to pentyl acetates) + 1-alcohols (C_1 to C_5) [6].

Acknowledgements

The authors acknowledge the support of Prof. H. C. Trivedi, head of the department for providing the laboratory facilities.

References

[1] Sastry, N. V. and Raj, M. M. (1995). *Thermochim. Acta*, **257**, 39.
[2] Sastry, N. V. and Raj, M. M. (1996). *Ind. J. Chem.*, **35A**, 49.
[3] Sastry, N. V. and Valand, M. K. (1996). *J. Chem. Eng. Data.*, **41**, 1426.
[4] Ortega, J., Pena, J. A. and Paz-Andrade, M. I. (1986). *Aust. J. Chem.*, **39**, 1685.
[5] Ortega, J. and Susial, P. (1989). *Can. J. Chem.*, **67**, 1120.
[6] Quin, A., Hoffman, D. E. and Munk, P. (1993). *Collect. Czech. Chem. Commun.*, **58**, 2625.
[7] Diaz Pena, M. and Tardajos, G. (1979). *J. Chem. Thermodyn.*, **11**, 441.
[8] Ortega, J. (1982). *J. Chem. Eng. Data.*, **19**, 312.