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Densities and Viscosities of 1,1,1-Trichloroethane + Paraffins and + Cycloparaffins at 298.15 K

Lorenzo De Lorenzi, Maurizio Fermeglia,* and Giovanni Torriano

DICAMP, Dipartimento di Ingegneria Chimica, dell'Ambiente e delle Materie Prime, Università di Trieste,
Piazzale Europa 1, I-34127 Trieste, Italy

Density and kinematic viscosity have been measured with a vibrating tube densimeter and an Ubbelohde capillary viscometer for binary mixtures of 1,1,1-trichloroethane and six paraffins, hexane, heptane, octane, decane, dodecane, and hexadecane, and five cycloparaffins, cyclohexane, methylcyclohexane, ethylcyclohexane, propylcyclohexane, and butylcyclohexane, at atmospheric pressure and 298.15 K. The dynamic viscosity, excess volume, and viscosity deviation function have been obtained from the density and kinematic viscosity results. The results have been correlated with a polynomial expression for the excess volume and with a recently published model for the mixture viscosity. Parameters for such models are reported.

Introduction

Mixtures of organic liquids often show strong deviations from ideality as regards density and viscosity. Predicting deviations is important in industrial fields, where different solvents are to be mixed. Several methods are available for correlating density and viscosity for binary mixtures, but unfortunately they rely on the availability of binary (or higher) interaction parameters. Recently, new models for the prediction of the viscosity of mixtures have been developed, some of which are based on the group contribution concept (*1*) and others of which are based on the molecular approach (*2*). The former are based on the principle that a liquid mixture is considered as a mixture of interacting functional groups; the description of the macroscopic properties of the mixture is, therefore, obtained by the knowledge of how each group interacts with the other groups present in the mixture. The latter models require binary interaction parameters for each binary system present in the multicomponent mixture, but no ternary (or higher) constants are generally needed.

The present work aims at expanding the range of mixtures available for testing and refining the above models, supplying data of the density, excess volume, kinematic and dynamic viscosity, and viscosity deviation function for 11 binary systems, containing 1,1,1-trichloroethane mixed with paraffins or cycloparaffins.

Additionally, 1,1,1-trichloroethane (chlorothene) is a versatile solvent on account of its many favorable characteristics, which make it suitable for various practical applications in different fields, e.g., in the paint and varnish industry, in inks, etc. For chlorothene properties see ref 3.

Experimental Section

Materials. All the solvents used were Aldrich, purity >99 mol %, used as received, without further treatment. The purities of nitrogen and water employed for the calibration of the instruments were 99.9999 and 99.9 mol %, respectively.

Apparatus. Densities were measured by a vibrating tube digital densimeter, Anton Paar, model DMA 602H - DMA 60, connected with an Heterofrig (Heto Birkerød) constant-temperature bath circulator, with a precision of ±0.01 K. Calibration of the apparatus and working procedures are described elsewhere (*4, 5*). The density estimated precision is higher than 3×10^{-5} g/cm^3.

Viscosities were measured by means of an Ubbelohde suspended-level capillary viscometer, coupled with a Schott electronic timer AVS 300, with a precision of ±0.01 s, and a Schott TA 20 - T 100 automatic diluting device. The Ubbelohde viscometer was immersed in a constant-temperature bath coupled with a Haake F3 thermostat, with a precision, experimentally verified, of ±0.02 K. Calibration of the apparatus and working procedures are described elsewhere (*4, 5*). The estimated precision in the kinematic viscosity measurement is approximately 1×10^{-4} mm^2/s.

Nitrogen and bidistilled water were employed to calibrate the densimeter. For the calibration of the viscometer the Poulten Selfe & Lee standard oil K5 was employed.

Procedure. The mixtures for the density measurements were prepared by mass. A Mettler balance with a precision of 3×10^{-5} g and air-tight bottles were used. Details on the experimental procedure are reported in refs 4 and 5. The possible error in the mole fraction is estimated to be lower than 5×10^{-5}. Repeated experiments of V^E indicated the reproducibility to be around 2×10^{-3} g/cm^3.

The mixtures for the kinematic viscosity measurements were obtained by volume. The calibration of the Schott T 20 - T 100 automatic diluting device indicated that the possible error in the mole fraction is approximately 2×10^{-3}.

Results and Correlations

All the measurements were made at 25 °C and at atmospheric pressure. A comparison between literature values (*3, 6-8*) and the pure component values measured in this work is reported in Table 1. The data reported in Table 1, which are the result of multiple experiments with low standard deviations, agree well with the literature data, thus allowing us to conclude that the calibrations of the instruments and the experimental procedure are correct.

Results for binary mixtures are shown in Tables 2-12 where density d (g·cm^{-3}) and kinematic viscosity ν (mm^2·s^{-1}) are the directly measured quantities. The dynamic viscosity η (mPa·s), excess volumes V^E (cm^3·mol^{-1}), and viscosity deviation function Δf (mm^2·s^{-1}) are derived quantities and were calculated by the following equations, respectively:

$$\eta = \nu d \tag{1}$$

$$V^E = \frac{x_1M_1 + x_2M_2}{d} - \frac{x_1M_1}{d_1} - \frac{x_2M_2}{d_2} \tag{2}$$

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* To whom correspondence should be addressed.

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Table 1. Comparison between Measured and Literature Data for Density d and Viscosity η of Pure Components at 298.15 K

solvent	$d/(\mathrm{g\cdot cm^{-3}})$ (this work)	$d/(\mathrm{g\cdot cm^{-3}})$ (lit.[a])	$d/(\mathrm{g\cdot cm^{-3}})$ (lit.[b])	$\eta/(\mathrm{mPa\cdot s})$ (this work)	$\eta/(\mathrm{mPa\cdot s})$ (lit.[c])	$\eta/(\mathrm{mPa\cdot s})$ (lit.[b])	$\eta/(\mathrm{mPa\cdot s})$ (lit.[d])	$\eta/(\mathrm{mPa\cdot s})$ (lit.[e])
1,1,1-trichloroethane	1.329 32	1.329 9	1.329 9	0.7917	0.795			
hexane	0.654 87	0.654 84	0.654 89	0.2965	0.2942	0.2968	0.2948	0.2949
heptane	0.679 48	0.679 46	0.679 50	0.3903	0.3967	0.3906	0.3893	0.3890
octane	0.698 56	0.698 62	0.698 54	0.5092	0.5151	0.5128	0.5095	0.5092
decane	0.726 09	0.726 35	0.726 35	0.8496	0.8614	0.8406	0.8493	0.8498
dodecane	0.745 87	0.745 18	0.745 18	1.3528	1.378	1.370	1.3579	1.3585
hexadecane	0.770 30		0.769 94	3.0248		3.052		
cyclohexane	0.773 71	0.773 89	0.773 87	0.8882	0.898	0.8923	0.8940	
methylcyclohexane	0.764 83	0.765 06	0.765 02	0.6810	0.685	0.6765		
ethylcyclohexane	0.783 82	0.783 90	0.783 84	0.7842	0.787	0.7847		
propylcyclohexane	0.789 74		0.789 68	0.9372		0.931		
butylcyclohexane	0.795 46		0.795 46	1.1922		1.204		

[a] Data from ref 3. [b] Data from ref 6. [c] Data calculated from ref 3. [d] Data interpolated according to eq 3 and Table 3 of ref 7. [e] Data from ref 8.

Table 2. Experimental Results for x 1,1,1-Trichloroethane + $(1-x)$ Hexane at 298.15 K

x	$d/(\mathrm{g\cdot cm^{-3}})$	$V^E/(\mathrm{cm^3\cdot mol^{-1}})$	x	$\nu/(10^{-6}\ \mathrm{m^2\cdot s^{-1}})$	$\Delta f/(10^{-6}\ \mathrm{m^2\cdot s^{-1}})$	$\eta/(\mathrm{mPa\cdot s})$
1.0000	1.329 31	0.000	1.000	0.5956	0.0000	0.7917
0.8087	1.167 87	0.159	0.906	0.5459	−0.0303	0.6810
0.7002	1.084 60	0.223	0.850	0.5236	−0.0418	0.6290
0.6015	1.013 54	0.253	0.750	0.4927	−0.0543	0.5529
0.4897	0.937 57	0.286	0.746	0.4916	−0.0547	0.5501
0.3968	0.878 17	0.276	0.650	0.4709	−0.0591	0.4933
0.2956	0.816 59	0.265	0.599	0.4625	−0.0594	0.4679
0.2886	0.812 50	0.260	0.499	0.4504	−0.0566	0.4250
0.1953	0.758 97	0.202	0.399	0.4430	−0.0504	0.3896
0.1014	0.707 67	0.117	0.299	0.4398	−0.0413	0.3599
0.0000	0.654 87	0.000	0.197	0.4404	−0.0297	0.3346
			0.098	0.4445	−0.0161	0.3137
			0.000	0.4528	0.0000	0.2965

Table 3. Experimental Results for x 1,1,1-Trichloroethane + $(1-x)$ Heptane at 298.15 K

x	$d/(\mathrm{g\cdot cm^{-3}})$	$V^E/(\mathrm{cm^3\cdot mol^{-1}})$	x	$\nu/(10^{-6}\ \mathrm{m^2\cdot s^{-1}})$	$f/(10^{-6}\ \mathrm{m^2\cdot s^{-1}})$	$\eta/(\mathrm{mPa\cdot s})$
1.0000	1.329 33	0.000	1.000	0.5956	0.0000	0.7917
0.8975	1.233 96	0.168	0.849	0.5511	−0.0384	0.6570
0.7945	1.147 31	0.295	0.839	0.5488	−0.0402	0.6497
0.6795	1.059 55	0.407	0.765	0.5375	−0.0489	0.6043
0.5904	0.997 52	0.453	0.747	0.5351	−0.0507	0.5937
0.4941	0.935 22	0.493	0.648	0.5273	−0.0554	0.5470
0.3942	0.875 76	0.463	0.576	0.5248	−0.0559	0.5186
0.2994	0.823 50	0.387	0.549	0.5246	−0.0555	0.5090
0.1972	0.771 16	0.252	0.449	0.5262	−0.0517	0.4778
0.0915	0.720 40	0.153	0.352	0.5312	−0.0450	0.4527
0.0000	0.679 48	0.000	0.198	0.5456	−0.0289	0.4209
			0.000	0.5744	0.0000	0.3903

Table 4. Experimental Results for x 1,1,1-Trichloroethane + $(1-x)$ Octane at 298.15 K

x	$d/(\mathrm{g\cdot cm^{-3}})$	$V^E/(\mathrm{cm^3\cdot mol^{-1}})$	x	$\nu/(10^{-6}\ \mathrm{m^2\cdot s^{-1}})$	$\Delta f/(10^{-6}\ \mathrm{m^2\cdot s^{-1}})$	$\eta/(\mathrm{mPa\cdot s})$
1.0000	1.329 32	0.000	1.000	0.5956	0.0000	0.7917
0.8934	1.234 82	0.219	0.837	0.5841	−0.0305	0.6940
0.7701	1.136 49	0.407	0.800	0.5847	−0.0343	0.6778
0.6754	1.067 65	0.519	0.699	0.5906	−0.0406	0.6406
0.5604	0.991 31	0.552	0.600	0.6013	−0.0426	0.6113
0.4650	0.932 46	0.612	0.500	0.6149	−0.0420	0.5865
0.3683	0.877 83	0.507	0.500	0.6157	−0.0412	0.5871
0.2550	0.817 59	0.456	0.400	0.6322	−0.0381	0.5661
0.1861	0.783 51	0.352	0.301	0.6522	−0.0319	0.5488
0.0814	0.734 53	0.162	0.203	0.6745	−0.0237	0.5340
0.0000	0.698 56	0.000	0.103	0.7000	−0.0132	0.5209
			0.000	0.7289	0.0000	0.5092

Table 5. Experimental Results for x 1,1,1-Trichloroethane + $(1-x)$ Decane at 298.15 K

x	$d/(\mathrm{g\cdot cm^{-3}})$	$V^E/(\mathrm{cm^3\cdot mol^{-1}})$	x	$\nu/(10^{-6}\ \mathrm{m^2\cdot s^{-1}})$	$\Delta f/(10^{-6}\ \mathrm{m^2\cdot s^{-1}})$	$\eta/(\mathrm{mPa\cdot s})$
1.0000	1.329 33	0.000	1.000	0.5956	0.0000	0.7917
0.9042	1.222 51	0.308	0.828	0.6725	0.0036	0.7734
0.7955	1.122 41	0.562	0.699	0.7393	0.0097	0.7746
0.6905	1.041 35	0.711	0.598	0.7948	0.0140	0.7802
0.5961	0.980 50	0.742	0.498	0.8523	0.0170	0.7882
0.4813	0.915 84	0.746	0.397	0.9127	0.0182	0.7981
0.3810	0.867 05	0.664	0.297	0.9740	0.0169	0.8089
0.2932	0.829 02	0.564	0.199	1.0357	0.0131	0.8205
0.1838	0.786 81	0.375	0.101	1.1010	0.0079	0.8342
0.0000	0.726 09	0.000	0.000	1.1700	0.0000	0.8496

$$\Delta f = \nu - \nu^{\mathrm{id}}$$

$$\ln(\nu^{\mathrm{id}}M) = \sum x_j \ln(\nu_j M_j) \tag{3}$$

where x_j is the mole fraction of component j, M_j the molecular weight of component j, M the molecular weight of the mixture, d_j the density of component j, ν_j the kinematic viscosity of component j, and ν^{id} the ideal viscosity as defined in eq 3.

The composition dependence of the excess volume ($\mathrm{cm^3\cdot mol^{-1}}$) was fit to the following equation:

$$V^{\mathrm{E}}_{\mathrm{calc}} = x_1 x_2 \sum_{j=0}^{n-1} \alpha_j (x_1 - x_2)^j \tag{4}$$

where α_j are parameters and n is the number of polynomial coefficients. A modified Levenberg–Marquardt numerical algorithm was used to minimize the objective function, written in terms of the sum of the squares of the differences between experimental and calculated values, divided by the experimental values.

The parameters a_j for the mixtures are reported in Table 13, along with the standard deviations of the fit. The most appropriate order of the polynomial (eq 4) to be used has been determined by means of an F test at the 95% confidence level. The standard deviation for the excess volumes ($\mathrm{cm^3\cdot mol^{-1}}$) reported in Table 13 was evaluated with the following equation:

$$\sigma(V^{\mathrm{E}}) = \left[\sum \frac{(V^{\mathrm{E}}_{\mathrm{calc}} - V^{\mathrm{E}}_{\mathrm{exp}})^2}{N - n}\right]^{1/2} \tag{5}$$

where N is the number of points and n the number of parameters.

The model recently developed by Cao et al. (*2*) has been used for the regression of the experimental kinematic viscosity values. The model combines the Eyring theory of viscosity and the local composition concept and is applicable to both pure components and mixtures. A detailed description of the model is given in the original paper. Using this model gives the advantage that no ternary (or higher) parameters are needed for describing the multicomponent mixture behavior.

Table 6. Experimental Results for *x* 1,1,1-Trichloroethane + (1 − *x*) Dodecane at 298.15 K

x	d/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	x	ν/(10^{-6} m^2·s^{-1})	Δf/(10^{-6} m^2·s^{-1})	η/(mPa·s)
1.0000	1.329 31	0.000	1.000	0.5956	0.0000	0.7917
0.8233	1.155 17	0.508	0.869	0.7355	0.0489	0.8791
0.6662	1.038 83	0.737	0.800	0.8111	0.0702	0.9211
0.5480	0.967 69	0.788	0.699	0.9283	0.1007	0.9844
0.5410	0.963 92	0.772	0.597	1.0497	0.1239	1.0453
0.4408	0.912 18	0.780	0.495	1.1759	0.1386	1.1046
0.4391	0.911 42	0.767	0.394	1.3029	0.1411	1.1601
0.3374	0.865 88	0.607	0.291	1.4326	0.1289	1.2129
0.2536	0.831 91	0.492	0.193	1.5590	0.1018	1.2613
0.2527	0.831 51	0.504	0.000	1.8136	0.0000	1.3528
0.1259	0.785 82	0.259				
0.0000	0.745 87	0.000				

Table 7. Experimental Results for *x* 1,1,1-Trichloroethane + (1 − *x*) Hexadecane at 298.15 K

x	d/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	x	ν/(10^{-6} m^2·s^{-1})	Δf/(10^{-6} m^2·s^{-1})	η/(mPa·s)
1.0000	1.329 32	0.000	1.000	0.5956	0.0000	0.7915
0.9304	1.223 38	0.514	0.874	0.9228	0.1802	1.0675
0.8547	1.137 47	0.675	0.788	1.1721	0.3061	1.2616
0.7607	1.055 64	0.781	0.601	1.7730	0.5513	1.6943
0.7213	1.026 70	0.872	0.499	2.1085	0.6296	1.9151
0.5841	0.946 37	0.977	0.400	2.4465	0.6562	2.1285
0.4859	0.902 66	0.893	0.297	2.7962	0.6148	2.3445
0.3816	0.864 66	0.745	0.195	3.1561	0.4893	2.5671
0.2598	0.828 28	0.539	0.096	3.5073	0.2632	2.7799
0.0000	0.770 30	0.000	0.000	3.9269	0.0000	3.0248

Table 8. Experimental Results for *x* 1,1,1-Trichloroethane + (1 − *x*) Cyclohexane at 298.15 K

x	d/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	x	ν/(10^{-6} m^2·s^{-1})	Δf/(10^{-6} m^2·s^{-1})	η/(mPa·s)
1.0000	1.329 32	0.000	1.000	0.5956	0.0000	0.7917
0.8997	1.267 97	0.115	0.700	0.6788	−0.0313	0.7808
0.8012	1.209 31	0.190	0.601	0.7169	−0.0384	0.7839
0.7035	1.152 22	0.256	0.501	0.7619	−0.0431	0.7905
0.6011	1.093 71	0.302	0.400	0.8151	−0.0451	0.8007
0.4931	1.033 33	0.322	0.301	0.8765	−0.0437	0.8143
0.3958	0.980 04	0.319	0.202	0.9489	−0.0377	0.8323
0.2978	0.927 48	0.287	0.101	1.0408	−0.0220	0.8584
0.1853	0.868 36	0.215	0.000	1.1478	0.0000	0.8882
0.1002	0.824 43	0.135				
0.0000	0.773 71	0.000				

Table 9. Experimental Results for *x* 1,1,1-Trichloroethane + (1 − *x*) Methylcyclohexane at 298.15 K

x	d/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	x	ν/(10^{-6} m^2·s^{-1})	Δf/(10^{-6} m^2·s^{-1})	η/(mPa·s)
1.0000	1.329 30	0.000	1.000	0.5956	0.0000	0.7917
0.9046	1.261 26	0.079	0.744	0.6361	−0.0184	0.7345
0.8018	1.191 86	0.160	0.602	0.6674	−0.0240	0.7126
0.7058	1.130 42	0.248	0.502	0.6935	−0.0257	0.7009
0.6008	1.067 41	0.269	0.402	0.7232	−0.0257	0.6917
0.5991	1.066 41	0.268	0.302	0.7568	−0.0236	0.6853
0.4891	1.003 60	0.324	0.201	0.7957	−0.0189	0.6813
0.4748	0.995 77	0.324	0.000	0.8903	0.0000	0.6810
0.2965	0.902 59	0.282				
0.1838	0.847 97	0.195				
0.0909	0.805 13	0.096				
0.0000	0.764 83	0.000				

Table 10. Experimental Results for *x* 1,1,1-Trichloroethane + (1 − *x*) Ethylcyclohexane at 298.15 K

x	d/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	x	ν/(10^{-6} m^2·s^{-1})	Δf/(10^{-6} m^2·s^{-1})	η/(mPa·s)
1.0000	1.329 33	0.000	1.000	0.5956	0.0000	0.7917
0.9010	1.253 77	0.136	0.752	0.6580	−0.0177	0.7577
0.7977	1.181 84	0.235	0.599	0.7079	−0.0227	0.7503
0.7026	1.120 87	0.311	0.500	0.7451	−0.0239	0.7493
0.6005	1.060 37	0.368	0.399	0.7869	−0.0236	0.7510
0.5382	1.026 08	0.351	0.300	0.8326	−0.0213	0.7555
0.4932	1.002 18	0.347	0.201	0.8819	−0.0172	0.7621
0.3891	0.949 52	0.358	0.000	1.0005	0.0000	0.7842
0.2860	0.901 29	0.306				
0.2010	0.864 11	0.229				
0.0923	0.819 40	0.122				
0.0000	0.783 82	0.000				

Table 11. Experimental Results for *x* 1,1,1-Trichloroethane + (1 − *x*) Propylcyclohexane at 298.15 K

x	d/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	x	ν/(10^{-6} m^2·s^{-1})	Δf/(10^{-6} m^2·s^{-1})	η/(mPa·s)
1.0000	1.329 30	0.000	1.000	0.5956	0.0000	0.7917
0.8974	1.244 39	0.157	0.800	0.6823	−0.0012	0.8002
0.7841	1.161 81	0.293	0.700	0.7314	−0.0007	0.8097
0.6967	1.104 90	0.370	0.650	0.7578	−0.0002	0.8157
0.6891	1.100 19	0.378	0.600	0.7844	−0.0001	0.8219
0.6041	1.050 17	0.421	0.500	0.8406	0.0004	0.8361
0.5051	0.997 36	0.401	0.402	0.9000	0.0006	0.8521
0.4060	0.948 88	0.410	0.299	0.9640	−0.0013	0.8691
0.4023	0.947 13	0.418	0.249	0.9980	−0.0016	0.8789
0.2945	0.899 50	0.359	0.151	1.0697	0.0008	0.9018
0.2025	0.862 48	0.248	0.096	1.1090	−0.0013	0.9126
0.0000	0.789 74	0.000	0.000	1.1868	0.0000	0.9372

Table 12. Experimental Results for *x* 1,1,1-Trichloroethane + (1 − *x*) Butylcyclohexane at 298.15 K

x	d/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	x	ν/(10^{-6} m^2·s^{-1})	Δf/(10^{-6} m^2·s^{-1})	η/(mPa·s)
1.0000	1.329 31	0.000	1.000	0.5956	0.0000	0.7917
0.7772	1.147 27	0.330	0.812	0.7276	0.0191	0.8527
0.6160	1.046 78	0.430	0.700	0.8139	0.0288	0.8926
0.5217	0.996 53	0.465	0.600	0.8971	0.0357	0.9308
0.4774	0.974 76	0.479	0.499	0.9853	0.0399	0.9708
0.3950	0.937 40	0.420	0.398	1.0786	0.0407	1.0123
0.3013	0.898 66	0.338	0.298	1.1757	0.0374	1.0550
0.2113	0.864 72	0.256	0.198	1.2779	0.0294	1.0990
0.0000	0.795 46	0.000	0.098	1.3863	0.0171	1.1452
			0.000	1.4988	0.0000	1.1922

Attention is drawn to an error contained in the original paper (eq 17) where the cubic root of the free volume of component *i* is missing. According to the authors (*9*), setting the value of the free volume to 1 does not modify the model validity and the numerical results.

The pure component parameters required for the description of the mixture viscosity have been taken from the compilation of Cao et al. (*10*), and the binary parameters ($\Delta U_{12} = U_{12} - U_{22}$ and $\Delta U_{21} = U_{21} - U_{11}$) (cal·mol^{-1}) in the following equations have been estimated by fitting the experimental results:

$$\ln(\eta V) = \sum_{i=1}^{n} x_i \ln(\eta_i V_i) - \sum_{i=1}^{n} q_i n_i x_i \sum_{j=1}^{n} \vartheta_{ji} \ln \tau_{ji} \qquad (6)$$

$$\tau_{ij} = \exp\left\{-\frac{z}{2}\left[\frac{U_{ji} - U_{ii}}{RT}\right]\right\} \qquad (7)$$

An explanation of all the terms in eqs 6 and 7 is beyond the scope of this work; consequently, reference is made to ref 2. V is the molar volume of the mixture and V_j the molar volume of component j. The binary parameters (ΔU_{12} and ΔU_{21}) are the interaction potential energy parameters.

The standard deviations obtained in the fitting are generally satisfactory (see Table 13). The high standard deviation found for 1,1,1-trichloroethane + hexadecane may be due to the pure component parameters used. Indeed, an analysis of the deviation distributions gives the highest values in the hexadecane-rich concentration region. Nevertheless, we have maintained the hexadecane pure component parameters given by Cao et al., in order to directly use the binary interaction parameters obtained in this work, together with those reported by Cao et al. to describe multicomponent mixtures. The

Table 13. Values of the Coefficients and Relevant Standard Deviations for Eqs 4 and 6

	1,1,1-trichloroethane +					
coefficient	hexane	heptane	octane	decane	dodecane	hexadecane
			Equation 4			
a_0	1.1370	1.8305	2.2989	3.0053	3.1179	3.3900
a_1	−0.2145	0.0636	0.0431	0.7484	0.7861	1.8735
a_2	0.0209			−0.0495	−0.3489	1.8973
$\sigma/(\mathrm{cm^3{\cdot}mol^{-1}})$	0.00085	0.00405	0.00194	0.00017	0.00083	0.01468
			Equation 6			
$\Delta U_{12}/(\mathrm{cal{\cdot}mol^{-1}})$	-202.01	-155.93	88.27	60.81	94.04	-169.35
$\Delta U_{21}/(\mathrm{cal{\cdot}mol^{-1}})$	201.10	145.34	-60.99	-38.69	-58.42	203.90
$\sigma/(\mathrm{mm^2{\cdot}s^{-1}})$	0.000383	0.000181	0.000554	0.000698	0.000812	0.02542

	1,1,1-trichloroethane +				
coefficient	cyclohexane	methylcyhexane	ethylcyhexane	propylcyhexane	butylcyhexane
		Equation 4			
a_0	1.2798	1.2632	1.4671	1.6874	1.8411
a_1	−0.2164	−0.3500	0.0257	0.0956	0.3114
a_2	0.1451	−0.3148			−0.4172
a_3	0.1185	0.3022			
$\sigma/(\mathrm{cm^3{\cdot}mol^{-1}})$	0.00032	0.00264	0.00119	0.01378	0.00125
		Equation 6			
$\Delta U_{12}/(\mathrm{cal{\cdot}mol^{-1}})$	-190.91	-169.13	-177.71	-170.62	
$\Delta U_{21}/(\mathrm{cal{\cdot}mol^{-1}})$	238.30	195.19	206.35	198.49	
$\sigma/(\mathrm{mm^2{\cdot}s^{-1}})$	0.001133	0.000613	0.000808	0.001484	

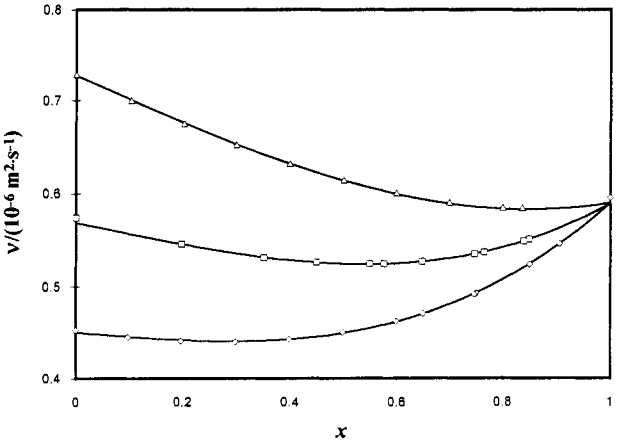

Figure 1. Kinematic viscosity for x 1,1,1-trichloroethane + $(1 - x)$ (◇) hexane, (□) heptane, and (△) octane.

viscosity standard deviation ($\mathrm{mm^2{\cdot}s^{-1}}$) reported in Table 13 was calculated with the following equation:

$$\sigma_\nu = \left[\sum \frac{(\nu^{\mathrm{calc}} - \nu^{\mathrm{exp}})^2}{N-2}\right]^{1/2} \qquad (8)$$

Discussion

Density is a monotonic function of the composition for all the mixtures considered. The curves of kinematic viscosity versus mole fraction for mixtures containing hexane, heptane, and octane show a minimum. This minimum falls at increasing mole fraction of 1,1,1-trichloroethane, starting from the hexane up to the octane mixtures (Figure 1). No minimum is observed, on the other hand, from the decane up to the hexadecane mixtures and for the cycloparaffin mixtures. The cyclohexane mixtures show a singular behavior as regards both location and shape of the relevant curve (Figure 2).

As regards the excess volume and viscosity deviation function, peculiar behaviors can be recognized by grouping the various systems according to the different classes of hydrocarbons.

Excess volumes for $(1 - x)$ paraffins + x 1,1,1-trichloroethane are always positive and progressively increasing from the hexane up to the hexadecane, as is shown in Figure 3, where the continuous lines report the values of the excess volumes calculated with eq 2 and the relevant parameters reported in Table 13. The maxima in x increase starting from mixtures containing hexane up to the mixtures containing hexadecane.

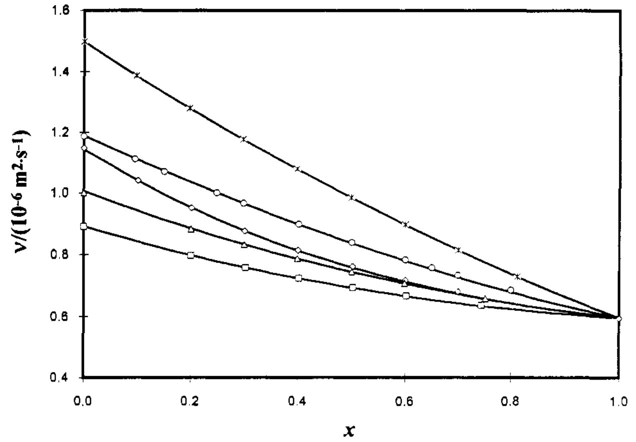

Figure 2. Kinematic viscosity for x 1,1,1-trichloroethane + $(1 - x)$ (◇) cyclohexane, (□) methylcyclohexane, (△) ethylcyclohexane, (○) propylcyclohexane, and (∗) butylcyclohexane.

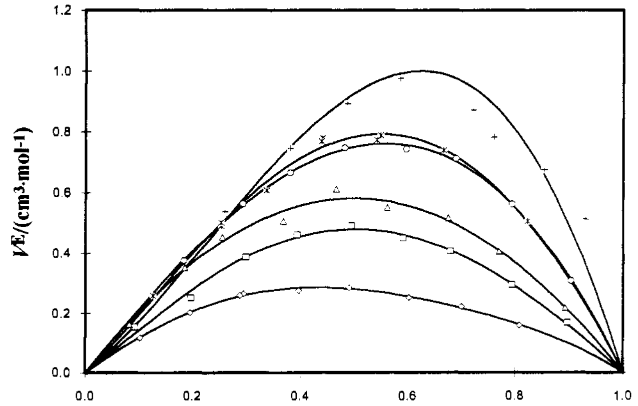

Figure 3. Excess volume for x 1,1,1-trichloroethane + $(1 - x)$ (◇) hexane, (□) heptane, (△) octane, (○) decane, (∗) dodecane, and (+) hexadecane.

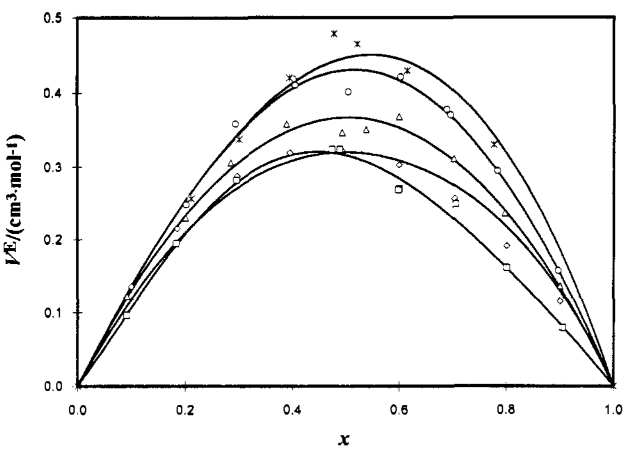

Figure 4. Excess volume for x 1,1,1-trichloroethane + (1 − x) (◇) cyclohexane, (□) methylcyclohexane, (△) ethylcyclohexane, (○) propylcyclohexane, and (∗) butylcyclohexane.

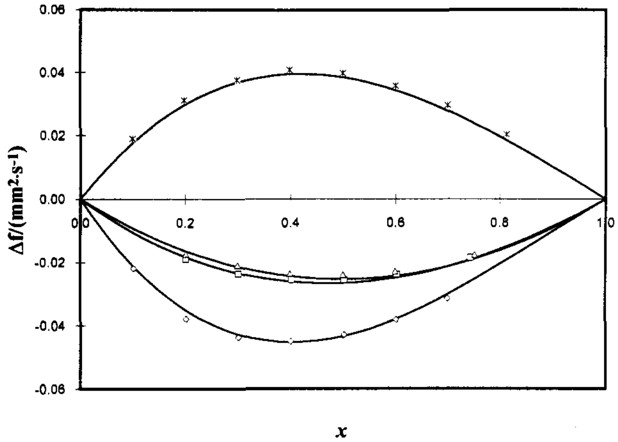

Figure 5. Viscosity deviation function for x 1,1,1-trichloroethane + (1 − x) (◇) cyclohexane, (□) methylcyclohexane, (△) ethylcyclohexane, and (∗) butylcyclohexane.

Viscosity deviation functions of paraffins show a peculiar behavior. The values are negative for the mixtures containing hexane, heptane, and octane and positive for the mixtures containing decane, dodecane, and hexadecane. A displacement of the minima and the maxima toward lower values of x at increasing number of C atoms of the paraffins is observed.

Excess volumes for cycloparaffins are always positive, the values being similar in magnitude (Figure 4), where the continuous lines have the same meaning as in Figure 3.

Viscosity deviation functions for cycloparaffins show unusual behavior (Figure 5). For the mixtures of cyclohexane the function is negative, and it is less negative for the mixtures containing methylcyclohexane. For the mixtures containing ethylcyclohexane the deviation is still negative and similar to that of the mixtures of methylcyclohexane; the deviation is negligible for propylcyclohexane (experimental points are not reported in Figure 5) and positive for the mixtures containing butylcyclohexane, with absolute values similar to those of the mixtures of cyclohexane.

The following considerations may be put forth to interpret the behaviors described in the preceding paragraphs.

The effect of mixing apolar paraffin molecules with polar 1,1,1-trichloroethane molecules lowers the total polarity of the system; correspondingly, a less compact structure develops. Hence, the free volume increases, and this brings about the positive excess volumes shown by all the mixtures. Since mixing takes place on molar ratios, increasing the number of the carbon atoms of the paraffins makes the phenomenon even more marked. Moreover, in addition to the effects of the variations of the total polarity of the systems, size effects must be taken into account in mixing the planar ribbon-shaped paraffin molecules with the rigid "pearlike" 1,1,1-trichloroethane molecules. The same situation, though quantitatively less marked, is found with the mixtures of cycloparaffins. In this instance, a six-membered ring replaces a trans planar six-membered (–CH_2–) structure. It is suggested that the presence of the ring structure allows a more favorable occupation of the space, involving a more compact packing of the molecules. So, the excess volumes for cycloparaffin mixtures are slightly smaller than those of the paraffins with a corresponding number of carbon atoms, with the exception of the hexane.

As far as the viscosity deviation function is concerned, flow involves alignment of the molecules. The smaller linear paraffins easily align under the shear rate. Moreover, paraffins diminish the system polarity compared with pure polar 1,1,1-trichloroethane, so their presence brings about a volume increase, and by virtue of their small volume and linear shape, they easily align under shear. This situation makes the general flow easier and gives rise to negative viscosity deviation functions. On the other hand, the opposite takes place with the longer paraffin chains. It is suggested that, in this case, the volume effects prevail over other effects and invert the previously described situation. Indeed, it can be thought that the longer planar ribbons of the higher paraffins with larger volumes align not so easily. This somewhat obstructs flow; hence, positive deviation functions are found, in spite of the presence of an appreciable positive excess volume. The same consideration may be extended to the case of the cycloparaffins.

Figures 1–5 report the comparison between the experimental data and the data calculated by means of the models and interaction parameters suggested. The agreement is good.

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