

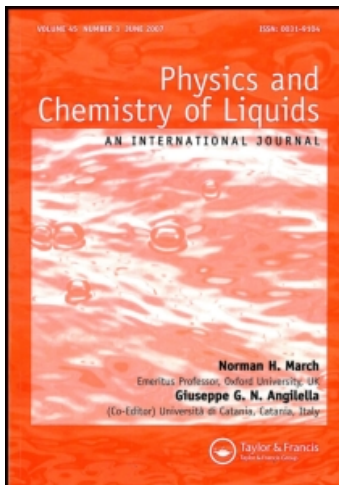
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Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

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To cite this Article Iloukhani, Hossein , Reddy, K. Dayananda and Rao, M. V. Prabhakara(1985) 'Excess Volumes of Trichloroethylene with Some Aliphatic and Alicyclic Ketones at 303.15K and 313.15K', *Physics and Chemistry of Liquids*, 14: 3, 181 – 188

To link to this Article: DOI: 10.1080/00319108508080981

URL: <http://dx.doi.org/10.1080/00319108508080981>

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Excess Volumes of Trichloroethylene with Some Aliphatic and Alicyclic Ketones at 303.15K and 313.15K

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(Received April 11, 1984)

Excess volumes on mixing for binary mixtures of trichloroethylene with aliphatic ketones and alicyclic ketones have been determined dilatometrically. The V^E data are reported over the complete mole fraction range at 303.15K and 313.15K. Aliphatic ketones include methylethylketone, methylpropylketone, diethylketone and alicyclic ketones are cyclopentanone and cyclohexanone. The measured V^E values are negative over the entire composition range. Temperature effect is also studied for all the binary systems. The observed values are interpreted in terms of (i) formation of hydrogen bond and (ii) dipole-induced dipole interactions between the dipole of the ketone and trichloroethylene.

1 INTRODUCTION

The present paper reports measurements of excess volumes for mixtures of trichloroethylene with methylethylketone, methylpropylketone, diethylketone, cyclopentanone and cyclohexanone at 303.15K and 313.15K. These measurements were made as part of continuing project on the thermodynamic properties of nonelectrolyte solution¹⁻³.

2 EXPERIMENTAL

Apparatus

Excess volumes were determined directly by the use of a dilatometer described by Reddy and Naidu.⁴ The mixing cell consisted of a *U*-tube of pyrex glass with mercury at the bottom to separate the two components.

One arm of the *U*-tube was fitted with a capillary tube and the other arm was closed with a ground-glass stopper. Seven dilatometers with different capacities were used to cover the entire composition range. The composition of the mixture was determined by direct weighing. The dilatometers were kept in a thermostat controlled to ± 0.01 K. The excess volumes are accurate to $\pm 0.003 \text{ cm}^3 \text{ mol}^{-1}$. The benzene + cyclohexane system at 298.15 K has been suggested as a standard for dilatometry. The measured excess volumes for this system are in good agreement with the earlier values reported in literature.⁵

TABLE I
Boiling points and densities of the pure compounds at 303.15K

Compound	Boiling point K		Density, ρ $\text{g} \cdot \text{cm}^{-3}$	
	Expt.	Lit. ^{5,7}	Expt.	Lit. ^{5,7}
Trichloroethylene	360.20	360.34	1.45134	1.4514
Methylethylketone	352.60	352.79	0.79448	0.79452
Methylpropylketone	373.40	373.55	0.79661	0.79656
Diethylketone	375.00	375.15	0.80460	0.80461
Cyclopentanone	403.70	403.80	0.93898	0.93902
Cyclohexanone	428.70	428.80	0.93760	0.93761

Materials

Trichloroethylene (BDH), methylpropylketone (Fluka), and cyclohexanone (BDH) were purified by the standard method described by Riddic and Bunger⁶. Methylethylketone (BDH) and diethylketone (BDH) were dried over potassium carbonate for 3 days, then boiled for 2 hours and distilled as reported by Naidu.⁷ Cyclopentanone (Fluka) was dried over anhydrous sodium sulphate for 2 days and then fractionally distilled. The purity of the compounds was checked by measuring densities and boiling points. The densities were measured by using a bicapillary pycnometer which gave an accuracy of 5 parts in 10^5 . The boiling points were measured using a Swietoslowski type ebulliometer which gave an accuracy of ± 0.2 K. The measured values are presented in Table I along with the literature values reported by Timmermans⁸ and Riddic *et al.*⁶

Results and Discussion

The excess volumes at 303.15K and 313.15K for trichloroethylene mixtures are listed in Table II and these are graphically represented in Figure 1–5. For each mixture, the excess quantities are fitted by the method of least-squares

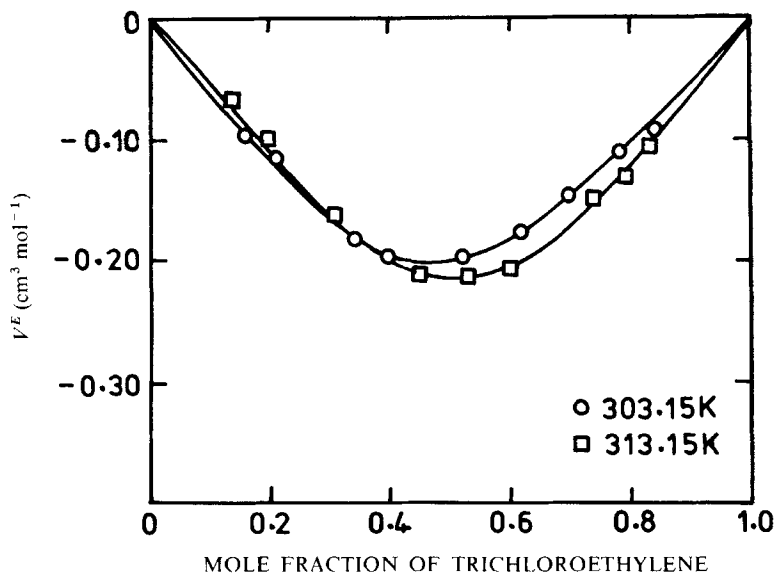


FIGURE 1 Excess volumes-composition curves for trichloroethylene with methylethylketone at 303.15K and 313.15K.

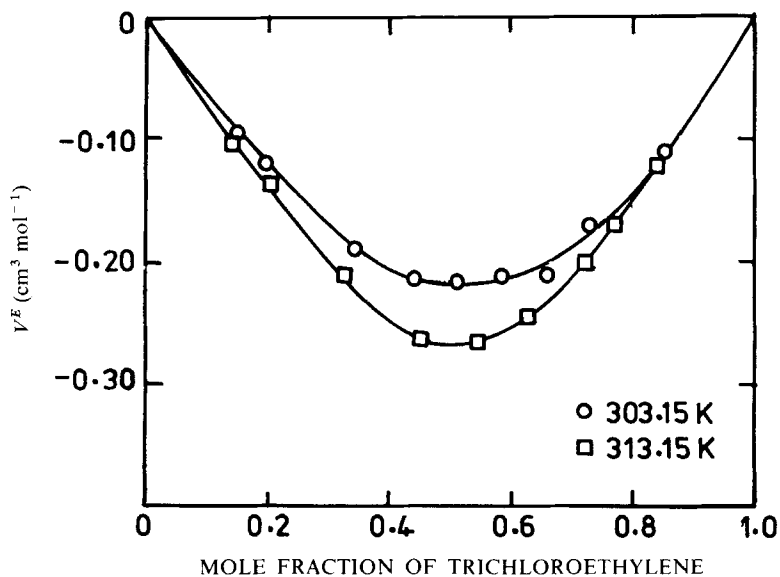


FIGURE 2 Excess volumes-composition curves for trichloroethylene with methylpropylketone at 303.15K and 313.15K.

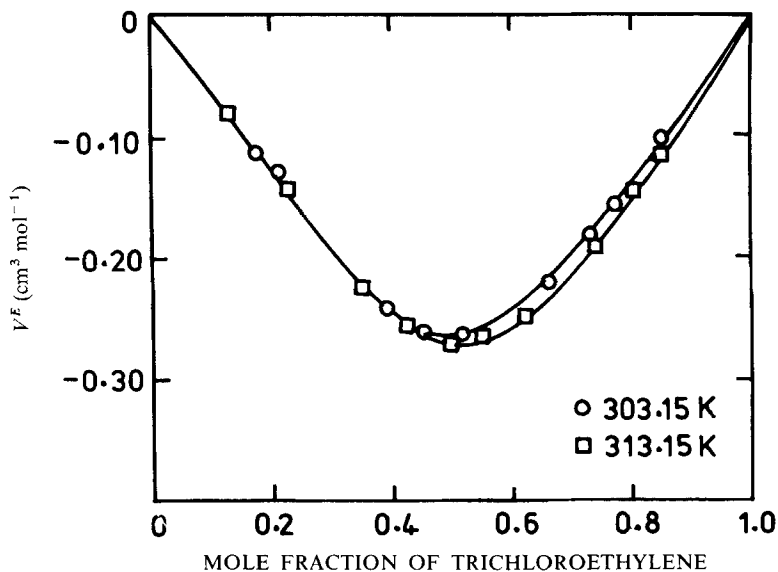


FIGURE 3 Excess volumes-composition curves for trichloroethylene with diethylketone at 303.15K and 313.15K.

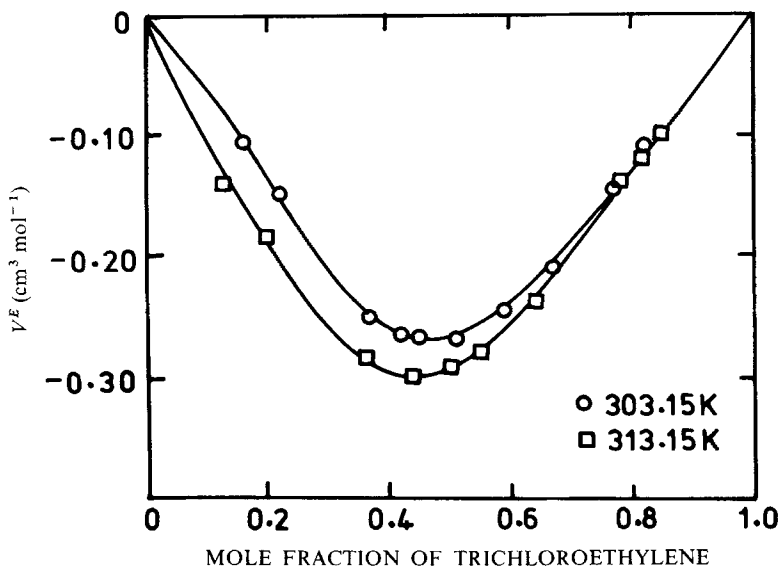


FIGURE 4 Excess volumes-composition curves for trichloroethylene with cyclopentanone at 303.15K and 313.15K.

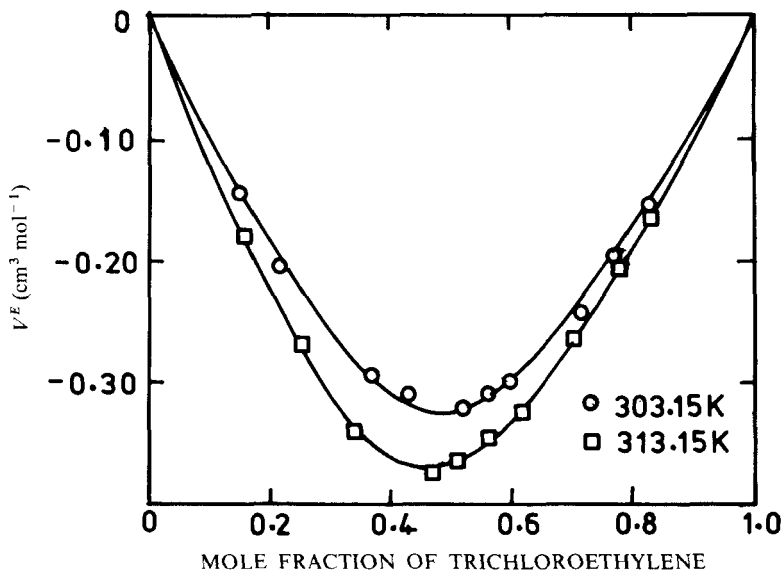


FIGURE 5 Excess volumes-composition curves for trichloroethylene with cyclohexanone at 303.15K and 313.15K.

TABLE II

Excess volumes V^E ($\text{cm}^3 \text{mol}^{-1}$) of trichloroethylene with ketones at 303.15K and 313.15K

Mole fraction of trichloroethylene x_A	V^E	Mole fraction of trichloroethylene x_A	V^E
Trichloroethylene + methylethylketone			
303.15K		313.15K	
0.1662	-0.097	0.1392	-0.066
0.2093	-0.124	0.2005	-0.098
0.3443	-0.182	0.3114	-0.159
0.4056	-0.194	0.4554	-0.217
0.5228	-0.198	0.5266	-0.223
0.6183	-0.177	0.6019	-0.212
0.7003	-0.148	0.7423	-0.152
0.7826	-0.119	0.7911	-0.129
0.8393	-0.095	0.8303	-0.107
Trichloroethylene + methylpropylketone			
0.1515	-0.094	0.1414	-0.097
0.2023	-0.123	0.2030	-0.135
0.3416	-0.190	0.3319	-0.212
0.4404	-0.224	0.4554	-0.260
0.5139	-0.232	0.5502	-0.262

TABLE II (continued)

Mole fraction of trichloroethylene x_A	V^E	Mole fraction of trichloroethylene x_A	V^E
0.5808	-0.226	0.6273	-0.245
0.6656	-0.210	0.7188	-0.204
0.7337	-0.178	0.7686	-0.171
0.8505	-0.110	0.8409	-0.120
Trichloroethylene + diethylketone			
303.15K		313.15K	
0.1730	-0.110	0.1379	-0.080
0.2119	-0.133	0.2314	-0.144
0.3889	-0.240	0.3553	-0.226
0.4503	-0.263	0.4313	-0.258
0.5237	-0.263	0.5051	-0.270
0.6616	-0.225	0.5519	-0.268
0.7352	-0.182	0.6226	-0.250
0.7713	-0.157	0.7389	-0.194
0.8505	-0.105	0.8039	-0.145
		0.8412	-0.115
Trichloroethylene + cyclopentanone			
0.1616	-0.108	0.1319	-0.124
0.2223	-0.150	0.2004	-0.185
0.3716	-0.249	0.3611	-0.285
0.4250	-0.263	0.4409	-0.303
0.4554	-0.268	0.5010	-0.294
0.5103	-0.273	0.5513	-0.280
0.5937	-0.248	0.6378	-0.240
0.6693	-0.213	0.7716	-0.146
0.7712	-0.147	0.8069	-0.120
0.8221	-0.113	0.8359	-0.101
Trichloroethylene + cyclohexanone			
0.1505	-0.147	0.1619	-0.180
0.2213	-0.207	0.2503	-0.269
0.3717	-0.294	0.3443	-0.340
0.4334	-0.310	0.4714	-0.375
0.5192	-0.321	0.5129	-0.368
0.5603	-0.313	0.5666	-0.348
0.6004	-0.300	0.6219	-0.324
0.7114	-0.246	0.7070	-0.265
0.7707	-0.200	0.7813	-0.208
0.8319	-0.157	0.8314	-0.166

TABLE III

Values of the parameters a_0 , a_1 , and a_2 of the Eq. (1) and the standard deviation $\sigma(V^E)$.

System	T	a_0	a_1	a_2	σ
	K				
Trichloroethylene + methylethylketone	303.15	-0.7883	0.0357	0.2004	0.005
	313.15	-0.8747	-0.1231	0.4858	0.004
Trichloroethylene + methylpropylketone	303.15	-0.9205	-0.1068	0.2584	0.002
	313.15	-1.0382	-0.0754	0.4281	0.003
Trichloroethylene + diethylketone	303.15	-1.0531	-0.0611	0.6029	0.003
	313.15	-1.0543	-0.1229	0.6263	0.006
Trichloroethylene + cyclopentanone	303.15	-1.0796	0.0515	0.7083	0.004
	313.15	-1.1812	0.3056	0.5826	0.003
Trichloroethylene + cyclohexanone	303.15	-1.2728	0.0433	0.3147	0.002
	313.15	-1.4704	0.1619	0.4967	0.006

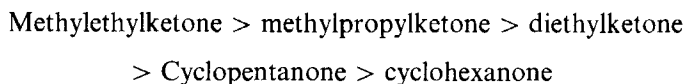
using the polynomial form:

$$V^E = x_A(1 - x_A) \sum_{i=0} a_i(2x_A - 1)^i \quad (1)$$

where x_A refers the mole fraction of trichloroethylene. The coefficients a_i and corresponding standard deviation σ are given in Table III. The binary mixtures formed by trichloroethylene + ketones have negative values of V^E over the entire range of composition at both the temperatures.

In these systems the curves are symmetrical and the maxima V^E value is around 0.5 mole fraction.

The numerical values of the excess volumes at both the temperatures of interest for the trichloroethylene with the ketones decrease in the order:



The V^E values for the systems methylpropylketone and cyclohexanone with trichloroethylene become more negative with increase in temperature and there is no temperature effect for the remaining systems. The observed V^E values are explained qualitatively in terms of (i) formation of hydrogen bonding between trichloroethylene and ketones, (ii) dipole-induced dipole interactions between the dipole of the ketone and trichloroethylene.

Acknowledgement

One of the authors (Hossein Iloukhani) is thankful to the University authorities for providing the necessary facilities to carry out the work.

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