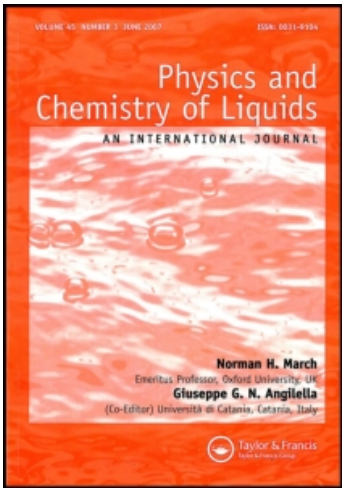

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Excess Volumes of 1,1,1-Trichloroethane with Normal Alkanols at 303.15 K

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To cite this Article Srinivasulu, U. and Naidu, P. R.(1989) 'Excess Volumes of 1,1,1-Trichloroethane with Normal Alkanols at 303.15 K', Physics and Chemistry of Liquids, 19: 3, 151 — 154
To link to this Article: DOI: 10.1080/00319108908030613
URL: http://dx.doi.org/10.1080/00319108908030613

Phys. Chem. Liq., 1989, Vol. 19, pp. 151-154
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EXCESS VOLUMES OF 1,1,1-TRICHLOROETHANE WITH NORMAL ALKANOLS AT 303.15 K

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(*Received* 29 *December* 1987)

New experimental data for excess volume of five binary mixtures are reported at 303.15 K. The mixtures contain 1,1,1-trichloroethane as common component and 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, and 1-heptanol as noncommon components. V^E exhibits inversion in sign in all mixtures except that containing 1-pentanol. In this mixture V^E is positive over the whole range of composition. The results have been interpreted in terms of the relative strength of structure breaking and structure making effects.

KEY WORDS: Binary mixtures, excess volumes, structure breaking effects.

INTRODUCTION

A survey of literature showed that excess volumes for binary mixtures 1,2-dichloroethane with a homologous series of normal alkanols have been measured at 303.15 K. However, no effort has been made to measure excess volumes of binary mixtures of 1,1,1-trichloroethane with 1-alcohols. Hence we report here new data for excess volumes for five binary mixtures which included 1,1,1-trichloroethane as common component. The non-common components were 1-propanol, 1-butanol, 1-pentanol, 1-hexanol and 1-heptanol. The data afford an opportunity to study the influence of a third chlorine atom on the orientational factors which determine the sign and magnitude of the excess volume.

EXPERIMENTAL

Excess volumes were measured by using the dilatometer described by Rao and Naidu[2]. It contained two bulbs of different capacities, connected through U-tube in which mercury is used to separate the two components. One end of the first bulb was fitted with a capillary outlet (0.8 mm iD) and second bulb was fixed with ground-glass stopper. The values of excess volume were accurate to 0.003 $Cm^3\ mol^{-1}$.

All the chemicals used were of analytical grade and were further purified by the methods described by Riddick and Bunger[3].

1,1,1-Trichloroethane was washed with concentrated hydrochloric acid, 10% potassium carbonate solution and 10% sodium chloride solution. The sample was dried over calcium chloride and fractionated.

Table 1 Densities of pure components.

	Density g/Cm³	
Compound	*Expt.*	*Lit.*
1,1,1-Trichloroethane	1.32102	1.32096
1-Propanol	0.79571	0.79567
1-Butanol	0.80194	0.80206
1-Pentanol	0.80752	0.80764
1-Hexanol	0.81212	0.81201
1-Heptanol	0.81572	—

Table 2 Mole fraction of 1,1,1-Trichloroethane, x_1 and excess volumes, V^E, at 303.15 K.

x_1	V^E $Cm^3\ mol^{-1}$	ΔV^E $Cm^3\ mol^{-1}$	x_1	V^E $Cm^3\ mol^{-1}$	ΔV^E $Cm^3\ mol^{-1}$
1,1,1-Trichloroethane + 1-Propanol			1,1,1-Trichloroethane + 1-Hexanol		
0.0613	−0.014	−0.001	0.0667	−0.027	−0.003
0.1787	−0.028	−0.003	0.1672	−0.025	0.003
0.2116	−0.032	0.001	0.2522	−0.005	0.004
0.3212	−0.028	−0.003	0.3670	0.033	0.002
0.4618	0.016	0.000	0.4693	0.066	−0.002
0.5381	0.047	0.001	0.5650	0.092	−0.002
0.6887	0.110	0.000	0.6734	0.103	−0.004
0.7646	0.129	0.001	0.7139	0.109	0.003
0.8306	0.125	0.001	0.8229	0.081	0.005
0.8960	0.103	0.000	0.9167	0.052	0.003
1,1,1-Trichloroethane + 1-Butanol			1,1,1-Trichloroethane + 1-Heptanol		
0.0760	−0.031	0.001	0.1574	−0.008	−0.002
0.1437	−0.051	−0.003	0.2012	0.001	0.002
0.2093	−0.055	−0.001	0.3550	0.039	0.003
0.3241	−0.042	−0.001	0.4738	0.079	0.000
0.4250	−0.009	0.006	0.5244	0.099	0.001
0.5005	0.013	0.001	0.6578	0.136	0.003
0.6452	0.062	0.001	0.7328	0.145	0.002
0.6815	0.071	0.002	0.8876	0.106	−0.001
0.7949	0.087	0.002	0.9379	0.070	0.001
0.8448	0.082	0.002			
0.9207	0.059	0.001			
1,1,1-Trichloroethane + 1-Pentanol					
0.1600	0.020	−0.003			
0.2780	0.054	0.003			
0.3686	0.085	0.005			
0.4815	0.119	0.001			
0.5358	0.141	0.003			
0.5937	0.159	0.004			
0.6681	0.161	−0.007			
0.8036	0.151	−0.008			
0.9026	0.111	0.004			

$\Delta V^E = V^E$ (exp) − V^E (Eq. (1))

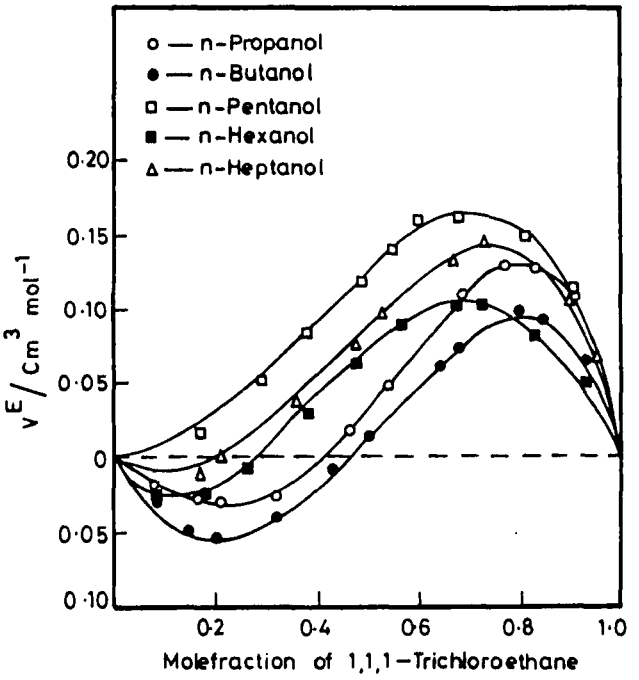

Figure 1 Molefraction vs. excess volume.

1-propanol (J. T. Baker) and 1-butanol (Qualigens) were refluxed over freshly ignited calcium oxide for six hours and distilled using a fractionating column. 1-Pentanol (Fluka) was dried over drierite and fractionally distilled. 1-Hexanol (B. D. H. England) were fractionally distilled. A fractionating column containing thirty theoritical plates was used in all cases. Purity of the samples was checked by comparing the measured densities with those reported in literature[3,4] (Table 1). The densities were measured by a bicapillary pycnometer which offered an accuracy of 3 parts in 10^5.

Table 3 Least square parameters and Standard deviation at 303.15 K.

System	a_0	a_1	a_2	$\sigma(\Delta V^E)$
1-Propanol	0.1250	0.8420	0.4939	0.001
1-Butanol	0.0461	0.7403	0.1736	0.002
1-Pentanol	0.5027	0.6742	0.2673	0.005
1-Hexanol	0.3083	0.6002	−0.2463	0.003
1-Heptanol	0.3544	0.7399	0.2358	0.002

RESULTS AND DISCUSSION

The excess volume data for the five binary mixtures are given in Table 2, and also are graphically presented in Figure 1. The dependence of excess volume on composition has been expressed by the polynomial

$$V^E = x_1x_2[a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \quad (1)$$

where a_0, a_1 and a_2 are the constants and x_1 and x_2 are the molefraction of 1,1,1-trichloroethane and alkanol respectively. The values of the parameters a_0, a_1 and a_2 were computed by the method of least squares and are given in Table 3.

The results in Table 2 show that excess volume exhibits inversion in sign in all mixtures except that containing 1-pentanol. Further, the negative values for V^E are observed upto molefraction 0.4 of 1,1,1-trichloroethane in mixtures of 1-propanol and 1-butanol. In mixtures of 1-hexanol and 1-heptanol V^E is found to be negative upto molefraction 0.25 of halogenated hydrocarbon.

Excess volumes of five mixtures may be attributed to structure breaking and structure making effects. Structure breaking effects includes: 1) depolymerisation of alcohols aggregates by halogenated hydrocarbon and 2) loss of dipolar association of the two components upon mixing. The structure making effect includes both interstitial accommodation of halogenated hydrocarbon in the aggregates of alcohols in mixtures rich in alcohols and possible hydrogen bond interaction of the type O—H—Cl between the unlike components. While structure breaking effect contributes to expansion in volume, the structure making effect leads to contraction in volume. The experimental results suggest the two effects compensate each other to different degrees in four mixtures containing 1-propanol, 1-butanol, 1-hexanol and 1-heptanol. Structure breaking effect, on the other hand, dominantes on the whole range of composition in the mixture containing the alcohol, 1-pentanol.

The excess volume data for mixture of 1,2-dichloroethane with five alcohols reported in the literature[1], are positive over the whole range of composition. V^E data included here for the mixture of the five alcohols with 1,1,1-trichloroethane, on the other hand, exhibit inversion in sign. The difference in trends of V^E data of the two groups of mixtures suggests that the third chlorine atom in ethane increases the hydrogen bond interaction between unlike molecules and interstitial accommodation of the halogenated hydrocarbon in the aggregates of alcohols in mixtures rich in alcohols.

References

1. Neetham. V. Choudary and Puligundla R. Naidu *Can. J. Chem.*, **59**, 2210-11 (1981).
2. M. V. P. Rao, P. R. Naidu, *Can. J. Chem.*, **52**, 788-90, 1976.
3. J. A. Riddick, W. S. Bunger, *Techniques of Chemistry*, 3rd ed. (Wiley-Interscience, New York, 1970).
4. J. Timmerman, *Physico-Chemical constants of pure organic compounds* (Elsevier Publishing Co., Amsterdam, 1950).