Volume Effects in Some Ternary Mixtures: Acetone + Carbon Tetrachloride + Cyclohexane & Acetone + Cyclohexane + Chloroform

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Excess molar volumes (V^E) of two ternary systems: (i) acetone + carbon tetrachloride + cyclohexane and (ii) acetone + cyclohexane + chloroform at 298.15K have been measured as a function of composition. The differences between the experimentally determined V^E values from and the sum of the binary contributions, illustrated as equivalue contours are found to be positive for the ternary system (i) and both positive and negative for system (ii).

The fact, that for the thermodynamic and related properties of multicomponent mixtures, the corresponding data of composite binaries may be used with advantage, has led to numerous publications[1-15] in the last two decades. In view of this and our interest in the study of excess properties of ternary mixtures[16-18] vis-a-vis their binary contributions, in this paper are reported the excess volumes of ternary systems: acetone + carbon tetrachloride + cyclohexane and acetone + cyclohexane + chloroform. The differences between experimentally determined excess volumes and sum of binary contributions, and termed as ternary volume effects have been determined and presented as equivalue contours on triangular plots.

Materials and Methods

The solvents used were of AR grade (BDH) except cyclohexane which was of LR grade (S. Merk), and were purified by literature, methods[19]. The purity of the solvents was checked by determining their densities and refractive indices which showed good agreement with the literature values[19,20]. The solvents were thoroughly degassed before use. The design and working of the three-limbed dilatometer, have been described elsewhere[17]. The estimated uncertainty in V^E for uncertainties in various measureable quantities[21] was of the order of ± 0.003 cm^3 mol^{-1}.

Results and Discussion

The experimental excess volumes of the two ternary systems, viz. acetone (1) + CCl$_4$$(2)$ + cyclohexane (3) and acetone (1) + cyclohexane (2) + chloroform (3) as a function of mol fractions of components (1) and (2) are summarized in Table 1. The V^E data of the composite binary mixtures, needed for the systems were searched from literature and satisfactory data were available

Table 1 — Excess Molar Volumes (V^E), Ternary Effects (ΔV^E), and their Corresponding Deviations $(\delta(\Delta V^E))$ of Two Ternary Systems at 298.15 K

x_1	x_2	V^E (cm^{3}mol^{-1})	ΔV^E (cm^{3}mol^{-1})	$10^3\delta(\Delta V^E)$* (cm^{3}mol^{-1})
(i) Acetone(1) + carbon tetrachloride 2) + cyclohexane(3)				
0.0681	0.6880	0.192	0.050	0
0.0722	0.6440	0.229	0.068	1
0.0869	0.6789	0.205	0.062	−0
0.0845	0.5875	0.284	0.097	2
0.0947	0.5505	0.302	0.097	−16
0.0975	0.3333	0.430	0.131	−2
0.0958	0.3102	0.435	0.130	2
0.1065	0.2885	0.460	0.131	−1
0.2406	0.6980	0.071	0.041	−6
0.2955	0.6493	0.070	0.055	−0
0.3279	0.6155	0.078	0.067	2
0.3698	0.0705	0.918	0.034	−11
0.3243	0.0725	0.894	0.049	−2
0.3750	0.5836	0.034	0.050	−3
0.4389	0.5170	0.043	0.063	1
0.4575	0.4945	0.053	0.067	0
0.5302	0.0650	0.919	0.017	−5
0.5956	0.3563	0.066	0.069	13
0.6414	0.3197	0.045	0.061	22
0.6326	0.3299	0.039	0.061	21
0.6095	0.3166	0.139	0.070	−1
0.6500	0.2838	0.126	0.061	6
0.6624	0.2818	0.100	0.061	14
0.6513	0.0654	0.784	0.010	1
0.7378	0.2318	0.020	0.031	13
0.7207	0.0509	0.702	0.001	0
0.3583	0.5955	0.039	0.045	−11
0.3962	0.3229	0.580	0.206	−2
0.4324	0.2568	0.649	0.174	−2
0.4072	0.3763	0.472	0.203	3
0.4302	0.2865	0.601	0.185	−3
0.3502	0.3768	0.540	0.223	−0
0.3102	0.3465	0.608	0.228	−3
0.3240	0.3764	0.569	0.236	7
0.1435	0.2308	0.550	0.136	−2
0.2108	0.5234	0.400	0.187	4
0.2348	0.2569	0.670	0.187	−4
				σ = 8

Table 1—Excess Molar Volumes (V^E), Ternary Effects (ΔV^E), and their Corresponding Deviations ($\delta(\Delta V^E)$) of Two Ternary Systems at 298.15 K— *Contd.*

x_1	x_2	V^E (cm³mol⁻¹)	ΔV^E (cm³mol⁻¹)	$10^3\delta(\Delta V^E)$ (cm³mol⁻¹)
		(ii) Acetone(1)+cyclohexane(2)+chloroform(3)		
0.1809	0.7436	0.700	−0.002	10
0.1230	0.5139	0.565	−0.030	7
0.1101	0.4524	0.528	−0.037	5
0.0487	0.1999	0.296	−0.010	16
0.0125	0.0513	0.086	0.010	13
0.2051	0.5070	0.632	−0.008	−2
0.1803	0.4507	0.548	−0.035	−17
0.1610	0.4060	0.503	−0.037	−8
0.0312	0.0333	0.061	0.016	17
0.4207	0.5136	0.983	0.019	−2
0.1884	0.2300	0.290	−0.033	−6
0.0960	0.1172	0.127	−0.023	4
0.0191	0.0233	0.034	0.008	10
0.4305	0.1944	0.447	0.102	−6
0.4127	0.1863	0.413	0.097	6
0.1593	0.0719	0.014	−0.029	−7
0.0886	0.5471	0.558	−0.033	6
0.0809	0.4993	0.546	−0.036	5
0.0720	0.4448	0.524	−0.038	4
0.0675	0.4170	0.505	−0.041	−0
0.0506	0.3127	0.424	−0.034	−0
0.0399	0.2465	0.348	−0.030	−5
0.0281	0.1740	0.277	−0.003	18
0.5157	0.2329	0.682	0.177	7
0.5197	0.2347	0.687	0.173	3
0.4009	0.2531	0.564	0.117	1
0.3892	0.2877	0.618	0.113	−3
0.4078	0.3062	0.683	0.127	−3
0.5718	0.1765	0.578	0.160	−5
0.5279	0.1793	0.545	0.159	6
				$\sigma = 9$

*Calculated using Eq. (14)

for three[9,22,23], of the five composite binaries. For the others, excess volumes were determined presently and the values are summarized in Table 2. The V^E values for all the systems were least square fitted to Eq. (1):

$$V^E/(cm^3\,mol^{-1}) = x(1-x)\sum A_i(1-2x)^{i-1} \quad \ldots (1)$$

The values of A_i alongwith the standard deviations σ's are summarized in Table 3.

To find the sum of the binary contributions, we propose a summation procedure in which it is assumed that when to a $(1+2)$ binary mixture containing components (1) and (2), component (3) is added, the three composite binarics are formed and the excess volume of the mixture may then be given by the summation expressed by Eq. (2).

$$V^E_{123} = [(n_1)_{12} + (n_2)_{12}]V^E_{12} + [(n_2)_{23} + (n_3)_{23}]V^E_{23}$$
$$+ [(n_3)_{31} + (n_1)_{31}]V^E_{31} \quad \ldots (2)$$

where $(n_i)_{ij}$ is the number of mol of the component (i) in the binary mixture (ij) so that

$$(n_1)_{12} + (n_1)_{13} = x_1 \quad \ldots (3)$$

and x_1 distributes itself proportionally between the components (2) and (3), i.e.

$$(n_1)_{12} = \frac{x_2}{x_2 + x_3} \cdot x_1 \quad \ldots (4)$$

and

$$(n_1)_{13} = \frac{x_3}{x_2 + x_3} \cdot x_1 \quad \ldots (5)$$

Table 2—Excess Molar Volumes (V^E) and Their Deviations ($\delta(V^E)$) from Eq. (1) at 298.15K

x	V^E (cm³mol⁻¹)	$10^4\delta(V^E)$ (cm³mol⁻¹)	x	V^E (cm³mol⁻¹)	$10^4\delta(V^E)$ (cm³mol⁻¹)
		(x)c-C₆H₁₂+(1−x)CHCl₃			
0.0409	0.0652	−5	0.5888	0.5819	13
0.2420	0.3890	−14.	0.5982	0.5740	−19
0.3135	0.4832	17	0.7667	0.4103	15
0.4427	0.5849	−18	0.9020	0.1840	−4
0.4965	0.5968	5	0.9347	0.1230	−4
0.5183	0.5960	−20			$\sigma = 16$
		(x)CHCl₃+(1−x)(CH₃)₂CO			
0.0850	0.0464	−13	0.4115	−0.0563	−25
0.1394	0.0559	3	0.4374	−0.0705	−22
0.1827	0.0510	−6	0.5830	−0.1290	25
0.2028	0.0480	9	0.6264	−0.1400	6
0.2043	0.0458	−9	0.7900	−0.1230	−18
0.2160	0.0450	16	0.9081	−0.05599	−3
0.2256	0.0397	−7	0.9150	−0.0540	12
0.3144	0.0038	29			$\sigma = 18$

Table 3—A_i Parameters of Eq. (1) for Composite Binary Mixtures at 298.15K

System	A_1	A_2	A_3	A_4	$10^4 \sigma$ (cm^{3}mol^{-1})	Ref.
$(CH_3)_2CO + CCl_4$	-0.4380	-0.4330	0.2660	—	10	22
$CCl_4 + c\text{-}C_6H_{12}$	0.6581	-0.0066	0.0279	—	27	23
$(CH_3)_2CO + c\text{-}C_6H_{12}$	4.482	-0.0540	0.7410	-0.4300	04	9
$c\text{-}C_6H_{12} + CHCl_3$	2.3922	0.1637	-0.6848	—	16	This work
$CHCl_3 + (CH_3)_2CO$	-0.4017	-0.9294	0.5125	0.1921	18	This work

Table 4—Parameters of Eq. (14) at 298.15K

System	ΔV^E (cm^3 mol)	σ
$(CH_3)_2CO + CCl_4 + c\text{-}C_6H_{12}$	$1 = 5.9953, 3 = 0.3320, 8 = -9.6597, 11 = -12.2227$	8
$(CH_3)_2CO + c\text{-}C_6H_{12} + CHCl_3$	$1 = 2.2170, 7 = -12.4579, 6 = -5.5116, 15 = -76.7176$	9

$(V^E)_{12}$ is the excess volume of the binary at mol fraction $(n_1)_{12}/[(n_1)_{12} + (n_2)_{12}]$ of the first component.

The advantage and unambiguity of Eq. (2) lies in its success to predict (i) correct V^E values for any of the three composite binaries, i.e. when component (3) is absent, $(n_1)_{12}$ and $(n_2)_{12}$ are just x_1 and x_2 and Eq. (2) takes the form (6)

$$V_{123}^E = (x_1 + x_2)V_{12}^E = V_{12}^E \qquad \ldots (6)$$

and (ii) correct V^E values for the equimolar mixture, where Eq. (2) can be shown to assume the form (7)

$$V_{123}^E = 1/3 (V_{12}^E + V_{23}^E + V_{31}^E) \qquad \ldots (7)$$

The need for such an equation over the other existing equations[1,7,24] is made relevant when a comparison is made of the predictions of various earlier methods.

Nissema[1] suggested an equation (Eq. 8), which

$$V_{123}^E = \sum x_i V_i \qquad \ldots (8)$$

like the one proposed presently gives correct V^E values for any of the three composite binaries in accordance with Eq. (6) and for the equimolar mixture in accordance with Eq. (7).

Redlich and Kister[24] proposed Eq. (9), to correlate the properties of a ternary mixture with those of its composite binaries.

$$V_{123}^E + x_1 x_2 \sum_{i=0}^{3}(A_i)_{12}(x_1 - x_2)^i + x_2 x_3 \sum (A_i)_{23}(x_2 - x_3)^i$$
$$+ x_3 x_1 \sum_{i=0}^{3}(A_i)_{31}(x_3 - x_1)^i \qquad \ldots (9)$$

It may be noted that Eq. (9) predicts the true value for any composite binary, and for the equimolar recipe, i.e. for $x_1 = x_2 = x_3 = 1/3$ it becomes,

$$V_{123}^E = 1/9 [(A_1)_{12} + (A_1)_{23} + (A_1)_{31})] \qquad \ldots (10)$$

Equation (10) thus predicts 4/3 times higher value, than that of the statistical sum for an equimolar mixture.

$$V_{123}^E = \tfrac{1}{3}[\tfrac{1}{4}(A_1)_{12} + (A_1)_{23} + (A_1)_{31}]$$
$$= \tfrac{1}{12}[(A_1)_{12} + (A_1)_{23} + (A_1)_{31}] \qquad \ldots (11)$$

Rastogi suggested an equation (Eq. 12) to sum up the binary contributions for a ternary mixture containing x_1, x_2 and x_3 mols of components (1), (2) and (3) respectively.

$$V_{123}^E = \tfrac{1}{2}[(x_1 + x_2)V_{12}^E + (x_2 + x_3)V_{23}^E + (x_3 + x_1)V_{31}^E] \qquad \ldots (12)$$

where V_{ij}^E (ij = 12, 23, or 31) is the excess volume of mixing per mol of the binary mixture having mol fraction $x_i/(x_i + x_j)$. Equation (12) gives V^E values for equimolar concentrations same as those given by Eq. (8) but under extremal conditions, i.e. when one of the components is absent, it predicts half the required value.

Thus the ternary effects as predicted by these two equations (Eqs 9 and 12) remain procedural functions and thus lack requisite quantitative significance.

The equations proposed by Nissema and the one proposed presently (Eq. 2) give similar values for equimolar and extremal mixtures. At other mol fractions the values agree within ±1% which is of the order of experimental error in ΔV^E determinations. One advantage of Eq. (2) is based upon the statistical formation of binaries in the ternary mixture, whereas in Nisseme's procedure the contribution of the overall binaries are added up, which no doubt for equimolar mixtures gives the same sum. Further the equation is easy to use in contrast to the required partial derivatives in Nissema's procedure.

Table 5—Values of Maximum Ternary Effects of Excess Molar Volumes at 298.15K

System	Mol fraction		V^E $(cm^3 mol^{-1})$	ΔV^E $(cm^3 mol^{-1})$
	x_1	x_2		
$(CH_3)_2CO + CCl_4 + c\text{-}C_6H_{12}$	0.30	0.37	0.59	0.23
$(CH_3)_2CO + c\text{-}C_6H_{12} + CHCl_3$	0.10*	0.37	0.46	-0.04
	0.57†	0.22	0.71	0.17

*Minimum, †Maximum

Fig. 1—Equivalue contours of ternary system, Acetone(1) + carbon tetrachloride (2) + cyclohexane (3)

For the presently studied two ternary systems, the summed up binary contributions for a ternary mixture (V^E_{123}) were subtracted from the corresponding experimental value (V^E),

$$\Delta V^E = V^E - V^E_{123} \qquad \ldots (13)$$

and the ternary volume effects (ΔV^E) thus obtained for various mixtures studied for the two systems using Eq. (13) are summarized in Table 1.

The estimated ternary effects for a system were fitted by the method of least squares to the general expression of the type (14)

$$\Delta V^E/cm^3 mol^{-1} = x_1 x_2 x_3 [D_0 + \sum D_i x_i$$

$$+ \sum D_{i+3}(x_i - x_{i+1}) + \sum D_{i+6}(x_i - x_{i-1})^2$$

$$+ \sum D_{i+9}x_{i+2}(x_i - x_{i+1})$$

$$+ \sum D_{i+12}(x_{i+2}(x_i - x_{i+1})^2] \qquad \ldots (14)$$
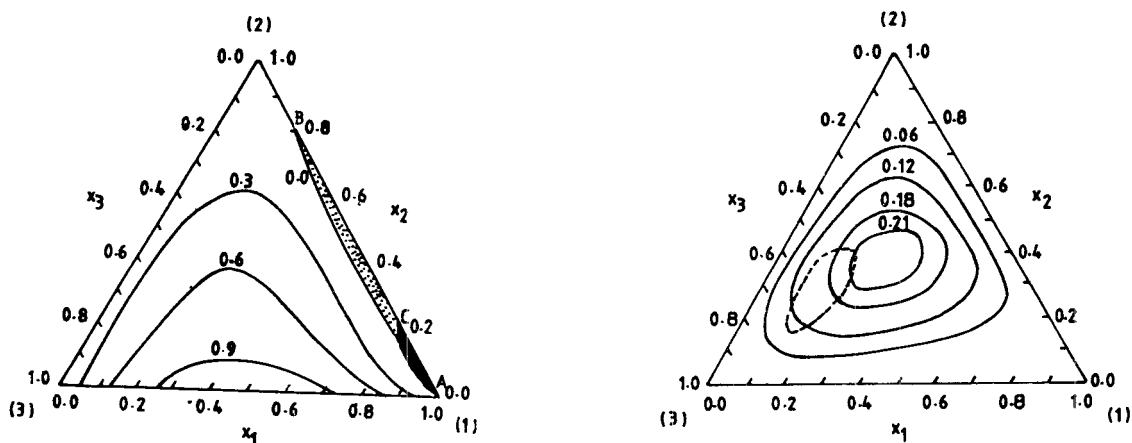
where $x_4 = x_1$ and $x_5 = x_2$, and parameters $D_0 \ldots D_{15}$ are the regression coefficients for sixteen functions at mol fractions x_1, x_2 and x_3.

Stepwise regression analysis was used to determine the D_i parameters of Eq. (14). After each addition of a parameter a statistical test (increase in

R_2) was applied and the new parameter was retained only if it stood the test. The D_i parameters along with the standard deviations are summarized in Table 4. Once the parameters were finalised, ΔV^E for any composition was then evaluated from Eq. (14) and the corresponding total property from Eq. (13). The deviations of recalculated ΔV^E values, $\delta(\Delta V^E\text{'s})$ and standard deviations σ's have also been included in Table 1. It may be seen that the $\delta(\Delta V^E)$ values are significantly smaller than the corresponding ΔV^E values thus indicating that ternary volume effects are positive for the first system and both positive and negative for the second system (Table 5). To have an understanding of the dependence of V^E and ΔV^E on mol fraction it was deemed appropriate to represent the data on equivalue contours, which for both the systems are illustrated in Figs. 1 and 2. The position of equivalue contours in triangular plots was computed by a method in which mol fraction of one of the components was kept constant while those of the other two were varied in steps of 0.05. The final refinement was attained by binary search method. The discussion of the observed excess volumes and their ternary effects for both the systems is given in the sequel.
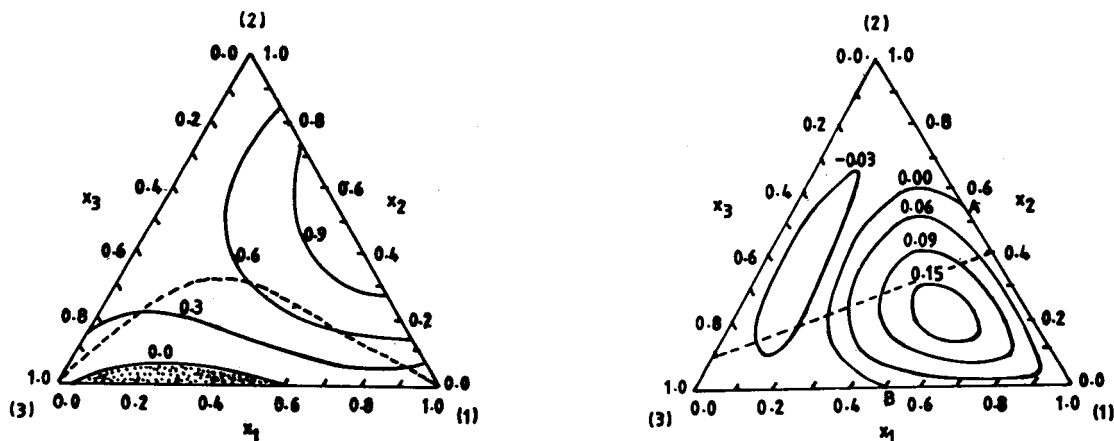
Fig. 2—Equivalue contours of ternary system, Acetone(1) + cyclohexane(2) + chloroform(3)

Acetone (1) + *carbon tetrachloride* (2) + *cyclohexane* (3)

This system consists of acetone as the polar component which is involved in n-π interaction with carbon tetrachloride thereby explaining the sigmoid dependence of V^E remaining negative for most of the concentration range. Small positive region is assignable to the breaking up of dipole-dipole interaction and H-bonds of enol form of acetone molecules. In the equivalue contours of this ternary system (Fig. 1a), negative (shaded) region does appear and affects the symmetrical disposition of contours around dominant binary, containing components (3) and (1). Such a behaviour is due to breaking up of the enol form of acetone molecules by cyclohexane. Small exothermic region observed for this system (darkend region) has been reported earlier. Not quite overlapping zero enthalpy contour (AC) with zero V^E contour (AB) is indicative of the absence of prevalent ideality; but of cancellation of contributing factors.

Ternary effects (ΔV^E) of this system are all positive (Fig. 1b), with the maximum displaced towards the binary containing components (2) and (3). The maximum lies around $x_1 = 0.30$ and $x_2 = 0.37$ and ΔV^E is as much as 40% of the corresponding V^E value. Similar disposition of ΔH^E contours have earlier been reported. For illustration, one contour corresponding to $\Delta H^E = 80$ J mol^{-1} for this system is shown in Fig. 1b. Positive signs of ΔV^E and ΔH^E indicate that when a (1 + 2) binary is diluted with component (3), the reduction in interaction is much more than that expected on statistical basis.

Acetone(1) + *cyclohexane*(2) + *chloroform*(3)

The (1 + 3) composite binary of this system has small sigmoid V^E dependence because of the formation of hetero H − bonded complex. Highly

positive V^E values for (1 + 2) binary system, as compared to those for (2 + 3) binary result in the orientation of the equivalue contours along it (Fig. 2a). Small negative region at low concentrations of acetone is also visible. This negative region is much more extended in the corresponding equienthalpic plot[16]. Zero H^E contour (given in dashes in Fig. 2a) has been included.

The ΔV^E plot of this system (Fig. 2b) shows both positive and negative regions separated by zero value contour, (line AB). The maximum and minimum lie around $x_1 = 0.57$, $x_2 = 0.22$ and $x_1 = 0.1$, $x_2 = 0.37$ respectively. No doubt the magnitude of ΔV^E as compared to corresponding V^E values at these positions is not very large (20 and 10% respectively) the behaviour is very much substantiated by the corresponding similar disposition of equienthalpic plots reported earlier[16]. For illustration, the zero enthalpy contour has been shown as dotted line in Fig. 2b. Lack of exact overlapping of ΔH^E and ΔV^E contours is suggestive of differential behaviour of contributing factors for these two properties. Contour AB in Fig. 2b represents the composition where additivity in binary contributions may be observed. It is apparent that when an equimolar acetone-chloroform mixture is diluted with cyclohexane an expansion in volume takes place till $x_{C_6H_{12}} = 0.45$ after which negative effects predominate. Thus, it appears that excess of cyclohexane favours the formation of H-bonded acetone-chloroform complex. However, further work needs to be done on other similar systems to arrive at useful generalizations.

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