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Excess Volumes of Mixing for Binary Mixtures of Diethyl Ether with Toluene, *o*-, *m*- and *p*-Xylenes

A.K. GUPTA* and C.K. YADAV†
University Department of Chemistry
L.N. Mithila University, Kameshwarnagar
Darbhanga-846008, India

Excess volumes of mixing (V^E) for binary mixtures of diethyl ether with toluene, *o*-, *m*- and *p*-xylene as a function of composition and temperature, have been determined dilatometrically. V^E values for mixtures have been found to be negative in sign and dependent on temperature. The measurements have been carried out at temperature 283.15 K, 293.15 K and 303.15 K.

INTRODUCTION

Excess volumes along with other excess thermodynamic properties for variety of binary liquid mixtures have been studied in order to examine current theories of solutions and the nature of molecular interactions.

Negative values of V^E for benzene-diethyl ether have been reported by Rastogi *et al.*[1] which provide strong evidence for the specific interaction between the components. These investigations have been extended to binary mixtures of diethyl ether with toluene, *o*-, *m*- and *p*-xylenes in order to examine the effect of increasing number of methyl groups and their relative positions in benzene ring, on the extent of molecular interaction. The results have been interpreted in the light of Flory's theory[2, 3] of binary mixtures of small non-polar molecules. A fairly good agreement has been found between theoretical and experimental values of V^E of binary mixtures at 303.15 K.

EXPERIMENTAL

Diethyl ether (Fluka AG, Puris, pa) was distilled fractionally three times and it was stored over sodium wire in brown bottles wrapped with black paper. Toluene (LR, BDH) was purified by prescribed method[4]. *o*-Xylene, *m*-xylene and *p*-xylene (Merck, Schuch ardt, pa) were fractionally distilled thrice and purified xylenes were separately stored over Na-wire in brown bottles.

The densities of the purified components were compared with the values obtained from literature and other workers. These were found in general agreement to ensure their purity.

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†P.G. Department of Chemistry, Purnea College, Purnea, (B.N.M. University), Madhepura, India.

Components	Temp.	Density (g/c.c.)	
		This work	Literature value[5–9]
Diethyl ether	303.15 K	0.70355	—
	293.15 K	0.71308	0.71352
Toluene	303.15 K	0.85840	0.85740
o-Xylene	303.15 K	0.87146	0.87154
m-Xylene	303.15 K	0.85622	0.85560
p-Xylene	303.15 K	0.85309	0.85230

Measurement of excess volume

The excess volume (V^E) is an important thermodynamic property which can be measured either by indirect method of measurement of densities or by direct dilatometric measurement of binary liquid mixtures. Different types of dilatometers have been used by different workers[9–12]. The dilatometer constructed by Rastogi, *et al*[1] was used for the purpose on account of its superiority over other models, because the chance of leakage of volatile liquids was minimised and complete mixing of components was ensured. It consisted of two closed bulbs in which liquids were introduced through the side tube.

The working of the dilatometer had been checked by making measurements for mixtures of cyclohexane and carbon tetrachloride at 303.15 K and data so obtained had been compared with that obtained by the earlier workers[1, 14] in Fig. 1.

V^E for the binary mixtures as a function of temperature and composition were determined by a dilatometer already checked by using the following relationship:

$$V^E = \pi r^2 \cdot \Delta h (n_1 + n_2)^{-1} \tag{1}$$

where r = radius of the capillary of vertical stem of dilatometer on mixing,

Δh = change in mercury levels in the capillary on mixing measured by cathetometer,

$n_1 + n_2$ = total number of moles in mixture.

RESULTS AND DISCUSSION

The values of V^E of binary mixtures have been recorded in Table-1. V^E data have been plotted in Fig. 2. The data were fitted in the analytical equation of the type

$$V^E/\text{c.c. mol}^{-1} = X_1X_2[A + B(X_1 - X_2) + C(X_1 - X_2)^2] \tag{2}$$

The constants A, B and C along with their standard deviation (σ_{V^E}) computed by the method of least square have been recorded in Table-2.

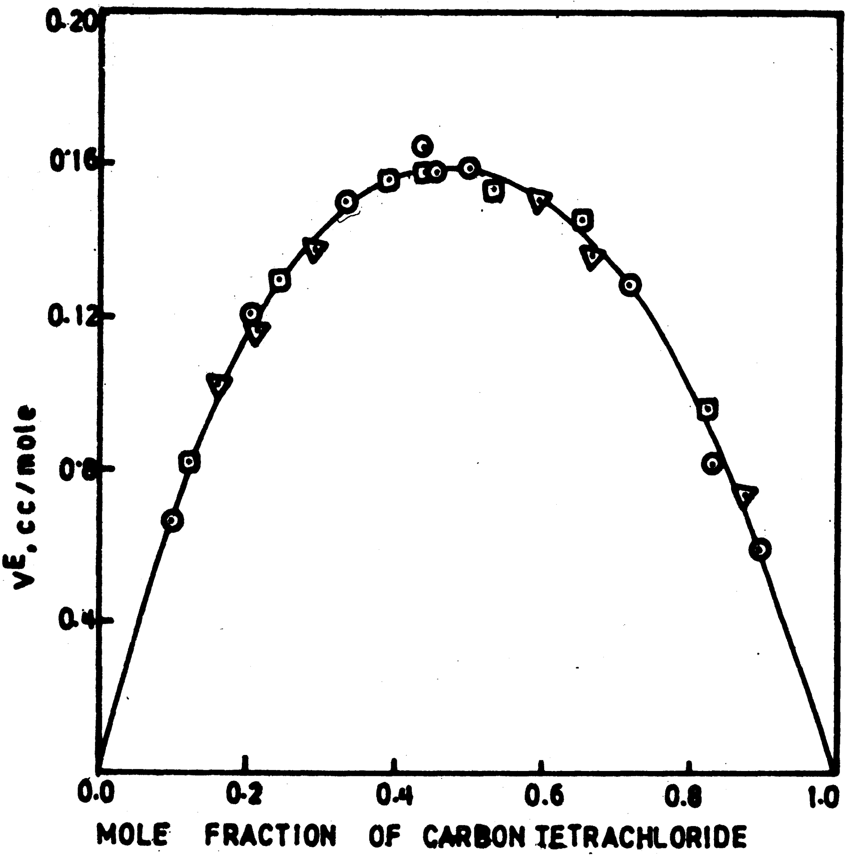

Fig. 1. Excess volumes of mixing for cyclohexane + carbon tetrachloride
⊙ This work, 30°C, △ Rastogi & Nath, 30°C (Ref. 14)
⊡ Rastogi & Yadava, 30°C (Ref. 1).

σ_{V^E} was calculated by the equation

$$\sigma_{V^E}/\text{c.c. mol}^{-1} = [\Sigma(\Delta V^E)^2/(m - n)]^{1/2} \qquad (3)$$

where, ΔV^E is the deviation in the observed values of excess volumes from that calculated from equation (2). 'm' is the number of observations and 'n' is the number of constants used in equation (2).

Temperature dependent V^E-equations for binary systems mentioned have been recorded in Table-3. The last column includes dV^E/dT for equimolal binary systems.

Despite the fact that diethyl ether is slightly polar molecule, the observed values of V^E have been examined in the light of statistical theory of binary liquid mixtures given by Flory *et al.*[2, 3]

TABLE-1

EXPERIMENTAL EXCESS VOLUMES V^E AT TEMPERATURE T FOR MOLE FRACTION X_1 OF DIETHYL ETHER

X_1	$-V^E$/c.c. mol^{-1}	X_1	$-V^E$/c.c. mol^{-1}
(X_1 diethyl ether + X_2 toluene) at T = 283.15 K			
0.1827	0.4501	0.2347	0.5361
0.3145	0.6400	0.4288	0.7095
0.4943	0.7355	0.5967	0.7200
0.6252	0.7112	0.7001	0.6501
0.8100	0.5106	0.9110	0.2707
(X_1 diethyl ether + X_2 toluene) at T = 293.15 K			
0.2042	0.5112	0.3999	0.7186
0.4050	0.7381	0.5088	0.7930
0.6070	0.7611	0.7831	0.5781
0.8043	0.5505	—	—
(X_1 diethyl ether + X_2 toluene) at T = 303.15 K			
0.0579	0.1439	0.2066	0.5150
0.2148	0.5637	0.4022	0.8353
0.5022	0.9002	0.5986	0.8531
0.7810	0.6057	0.8846	0.3637
(X_1 diethyl ether + X_2·*o*-Xylene) at T = 283.15 K			
0.1650	0.2601	0.2150	0.3632
0.3155	0.5201	0.5000	0.7234
0.6215	0.7508	0.7520	0.6501
0.8800	0.4078	—	—
(X_1 diethyl ether + X_2 *o*-xylene) at T = 293.15 K			
0.1050	0.1714	0.2050	0.3582
0.3028	0.5590	0.4055	0.7401
0.5030	0.8392	0.6500	0.8506
0.7721	0.6720	0.8550	0.4770
(X_1 diethyl ether + X_2 *o*-xylene) at T = 303.15 K			
0.2004	0.4025	0.2512	0.4898
0.4017	0.8140	0.5083	0.9500
0.8922	0.4150	—	—

X_1	$-V^E$/c.c. mol^{-1}	X_1	$-V^E$/c.c. mol^{-1}
(X_1 diethyl ether + X_2 *m*-xylene) at T = 283.15 K			
0.1690	0.2498	0.2237	0.3487
0.4115	0.6202	0.4550	0.6703
0.4899	0.7001	0.6500	0.7201
0.8150	0.4998	—	—
(X_1 diethyl ether + X_2 *m*-xylene) at T = 293.15 K			
0.2050	0.3205	0.3155	0.5178
0.4016	0.6601	0.5030	0.7508
0.6112	0.7810	0.7550	0.6545
0.9100	0.3073	—	—
(X_1 diethyl ether + X_2 *m*-xylene) at T = 303.15 K			
0.1876	0.2929	0.2087	0.3213
0.4010	0.7063	0.4512	0.7603
0.5630	0.8169	0.6635	0.9110
0.8854	0.3955	0.9218	0.2866
(X_1 diethyl ether + X_2 *p*-xylene) at T = 283.15 K			
0.1500	0.3490	0.3028	0.5899
0.4055	0.6898	0.5009	0.7456
0.7236	0.6652	0.8100	0.5301
0.9104	0.2996	—	—
(X_1 diethyl ether + X_2 *p*-xylene) at T = 293.15 K			
0.1936	0.4098	0.3002	0.6008
0.4100	0.7501	0.4974	0.8102
0.5210	0.8007	0.6050	0.8111
0.7702	0.6456	0.8500	0.4805
(X_1 diethyl ether + X_2 *p*-xylene) at T = 303.15 K			
0.1837	0.3310	0.3719	0.7794
0.4018	0.8326	0.5458	0.9905
0.5701	0.9941	0.7025	0.8884
0.8264	0.6165	0.9100	0.3284

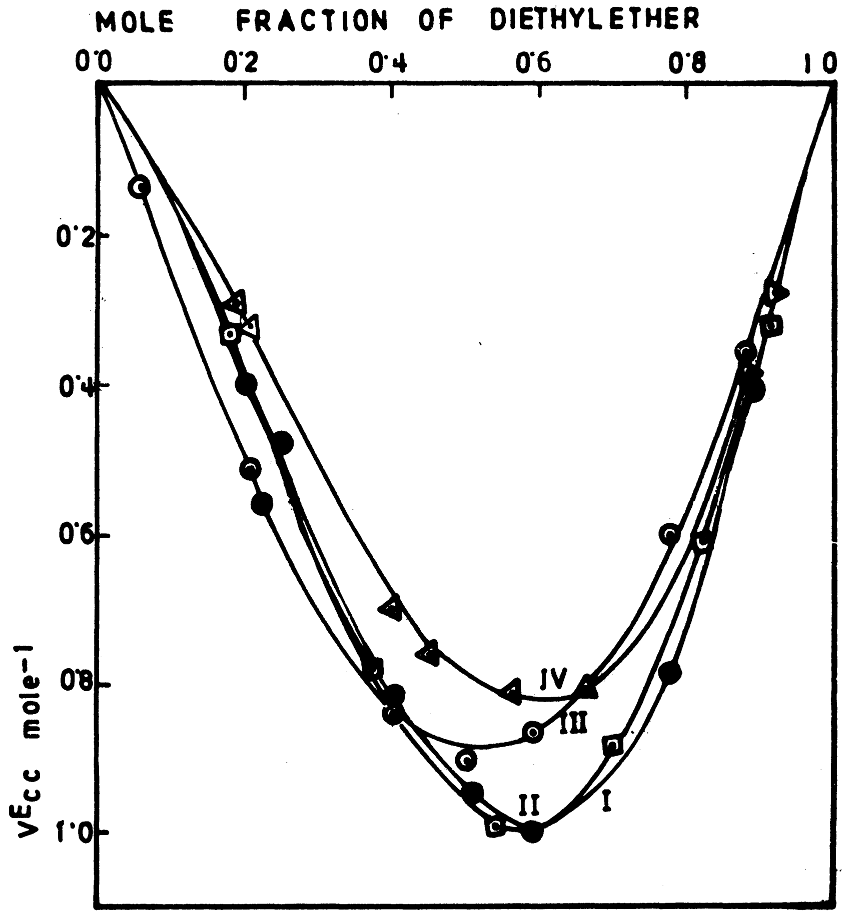

Fig. 2. Volume excess of mixing for: I. Diethyl ether + *o*-xylene, Experiemental point = ●. II. Diethyl ether + *p*-xylene, Experimental point = ⊡. III. Diethyl ether + toluene, Experiemntal point = ⊙. IV. Diethyl ether + *m*-xylene, Experimental point = ∆- curves calculated from the equation (Table-5) at 30°C.

Excess volume V^E is given by the equation:

$$V^E = \frac{X_1V_1/\tilde{v}_1 + X_2V_2/\tilde{v}_2)(\phi_1\tilde{v}_1 + \phi_2\tilde{v}_2)^{7/3}(\tilde{T} - \tilde{T}^\circ)}{\frac{4}{3} - (\phi_1\tilde{v}_1 + \phi_2\tilde{v}_2)^{1/3}} \qquad (1)$$

where X_1 and X_2 are mole fractions of 1st and 2nd component. $\tilde{v}_1$ and $\tilde{v}_2$ are their reduced volumes, ϕ_1 and ϕ_2 are their segment fractions, $\tilde{T}$ and $\tilde{T}^\circ$ are reduced and ideal reduced temperatures of binary systems.

$$\phi_2 = 1 - \phi_1 = \frac{X_2v_2^*}{X_1v_1^* + X_2v_2^*} \qquad (2)$$

TABLE-2
VALUES OF CONSTANTS A, B AND C OF BINARY MIXTURES AND STANDARD DEVIATIONS V^E AT TEMPERATURES T

Mixtures	T K	A	B	C	σ_{V^E}/c.c. mol^{-1}
Diethyl ether + toluene	283.15	-2.9560	-0.2401	-0.4540	0.0063
	293.15	-3.1309	-0.2838	-0.3545	0.0083
	303.15	-3.5934	-0.4068	+0.6961	0.0073
Diethyl ether + *o*-xylene	283.15	-2.8740	-1.0015	+0.5547	0.0092
	293.15	-3.3641	-1.4024	+0.8456	0.0088
	303.15	-3.8640	-1.8717	+1.1496	0.0174
Diethyl ether + *m*-xylene	283.15	-2.8028	-1.2291	+0.3527	0.0069
	293.15	-3.0068	-1.3498	+0.7200	0.0069
	303.15	-3.2008	-1.4704	+0.9123	0.0094
Diethyl ether + *p*-xylene	283.15	-3.0022	-0.6149	-0.3694	0.0074
	293.15	-3.2226	-0.8711	+0.1445	0.0071
	303.15	-3.8840	-1.6397	+1.6863	0.0075

$\tilde{T}$ and $\tilde{v}$ for pure liquids are given by

$$\tilde{T}_i = (\tilde{v}_i^{1/3} - 1)/(\tilde{v}_i)^{4/3} \tag{3}$$

$$(\tilde{v}_i^{1/3} - 1) = \frac{\alpha_i T/3}{(1 + \alpha_i T)} \tag{4}$$

where α_i = co-efficient of thermal expansion

T = temperature K.

$$v_i^* = v_i/\tilde{v}_i \quad \text{and} \quad T_i^* = T/\tilde{T}_i \tag{5}$$

$$\tilde{T}^\circ = \{(\phi_1\tilde{v}_1 + \phi_2\tilde{v}_2)^{1/3} - 1\}(\phi_1\tilde{v}_1 + \phi_2\tilde{v}_2)^{-4/3} \tag{6}$$

$$\tilde{T} = (\phi_1 p_1^* \tilde{T}_1 + \phi_2 p_2^* \tilde{T}_2)(\phi_1 p_1^* + \phi_2 p_2^* - \phi_1\theta_2 X_{12}). \tag{7}$$

where, $\theta_2 X_{12}$ is a pair-interaction parameter. Here we have made the approximation[14] that $\theta_2 X_{12} = 0$. Parameters for the pure components have been placed in Table-4.

The comparison has been made between calculated values (based on Flory's theory) and observed values of V^E for binary systems and have been recorded in Table-5.

Examination of Table-5 shows that even with approximation embodied in equation (7) Flory's theory predicts the sign correctly and magnitude of V^E to a fairly good degree for the systems mentioned. In absence of availability of the value of thermal pressure coefficient (γ) or k_T (isothermal compressibility) we could not be able to calculate V^E of (*o*-xylene-ether) theoretically using Flory's theory[2, 3]. Agreement between values of V^E (experimental) and V^E (theoretical) is excellent, despite the probability of uncertainty to some extent in the value of

TABLE-3

EQUATIONS FITTING THE EXPERIMENTAL DATA FOR EXCESS VOLUME V^E AT T (K)

Mixture	Equations fitting the experimental data	dV^E/dT
Diethyl ether + toluene	$\frac{V^E}{\text{c.c. mol}^{-1}} = X_1X_2[(6.10495 - 0.03187T) + (2.1378 - 0.00833T)(X_1 - X_2) + (-16.77316 + 0.05750T)(X_1 - X_2)^2]$	1.5262
Diethyl ether + *o*-xylene	$\frac{V^E}{\text{c.c. mol}^{-1}} = X_1X_2[(11.14352 - 0.04950T) + (11.32970 - 0.04351T)(X_1 - X_2) + (-7.86828 + 0.02974T)(X_1 - X_2)^2]$	2.7858
Diethyl ether + *m*-xylene	$\frac{V^E}{\text{c.c. mol}^{-1}} = X_1X_2[(2.82745 - 0.01989T) + (2.18736 - 0.01206T)(X_1 - X_2) + (-7.54079 + 0.02798T)(X_1 - X_2)^2]$	0.7068
Diethyl ether + *p*-xylene	$\frac{V^E}{\text{c.c. mol}^{-1}} = X_1X_2[(9.5558 - 0.04409T) + (13.97961 - 0.05124T)(X_1 - X_2) + (-29.76920 + 0.10321T)(X_1 - X_2)^2]$	2.3889

TABLE-4

PARAMETERS FOR THE PURE COMPONENT LIQUIDS AT 303.15 K

Liquid	$\frac{V}{\text{c.c. mol}^{-1}}$	$\frac{dX\ 10^3}{\text{dig}^{-1}}$	$\frac{\gamma}{\text{cal c.c.}^{-1}\ \text{dig}^{-1}}$	$\frac{\tilde{V}}{\text{c.c. mol}^{-1}}$	$\frac{V^*}{\text{c.c. mol}^{-1}}$	$\frac{T^*}{\text{OK}}$	$\frac{p^*}{\text{cal c.c.}^{-1}}$	$\tilde{T}$
Toluene	107.424	1.085	0.278	1.2684	84.69	5046	135.5	0.06007
o-Xylene	121.818	0.975	—	1.2459	97.77	5345	—	0.05671
m-Xylene	124.094	1.008	0.270	1.2527	99.06	5249	128.4	0.05775
p-Xylene	124.568	1.038	0.268	1.2589	98.95	5166	128.7	0.05868
Diethyl ether	105.350	1.395	0.161	1.3276	79.35	4465	86.0	0.06789

α (coefficient of thermal expansion) for diethyl ether, because the same has been calculated from our density data. The agreement between the two is remarkably better in both lower and higher mole fractions.

TABLE-5

COMPARISION OF EXPERIMENTAL EXCESS VOLUMES V^E WITH CALCULATED VALUES BASED ON FLORY'S THEORY AT 303.15 K

Mole fraction of diethyl ether (X_1)	V^E (Experimental) c.c. mol^{-1}	V^E (Calculated) c.c. mol^{-1}
	Diethyl ether + toluene	
0.2	–0.49579	–0.34211
0.5	–0.89835	–0.63834
0.8	–0.57390	–0.49020
	Diethyl ether + *m*-xylene	
0.2	–0.31841	–0.32048
0.5	–0.80025	–0.80907
0.8	–0.60074	–0.65576
	Diethyl ether + *p*-xylene	
0.2	–0.36689	–0.38486
0.5	–0.97100	–0.73167
0.8	–0.68172	–0.59065

A slight disagreement of the theory with the experiment in few cases may be due to orienting effects which exist in liquid mixtures on account of specific interactions between the two components in binary systems. Size effect[15] must be taken into account, since from toluene to xylenes there is increase in number of one—CH_3 group and change in their relative positions. Tables 1– 4 show that in the case of all the systems of diethyl ether with toluene, *o*-xylene, *m*-xylene and *p*-xylene, the value of V^E decreases with increasing temperature. This trend is in agreement with the results in binary systems of diethyl ether and benzene at 283.15 K, 193.15 K and 303.15 K by Rastogi *et al.*[1] There is similarity of weak hydrogen-bond formation between the two on account of the partial positive charge on H-atom of toluene and xylenes and negative charge on O-atom of diethyl ether. Murrel and Gil[15] have suggested a similar type of interaction between pyridine and benzene on the basis of NMR spectral studies.

The order of variation in the values of V^E for equimolal systems of diethyl ether with toluene, *o*-xylene, *m*-xylene and *p*-xylene at all temperatures 283.15 K, 293.15 K and 303.15 K is as follows:

Ether + *m*-xylene > Ether +toluene > Ether +*o*-xylene > Ether +*p*-xylene.

Combining these results with those of Rastogi, *et al*[1] the following trend has been found:

V^E : Ether + benzene > Ether +toluene > Ether + xylenes.

This supports that interactions vary almost regularly with increasing number of methyl groups in aromatic ring. Difference in magnitudes of V^E for systems of diethyl ether with xylenes may be due to different relative positions of methyl groups in the benzene ring.

The negative values of V^E are observed in all binary systems under investigation at all temperatures mentioned above. The various types of interactions that are operating between molecules in different systems are dispersion forces which makes positive contribution which must be superseded in these systems by negative contributing factors like charge transfer, H-bonding, dipole-dipole and dipole-induced dipole interactions etc. as suggested by different authors[17, 18]

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