Asian Journal of Chemistry Vol.9, No.3 (1997), 493–500

Excess Volumes Mixing for Binary Liquid Mixtures of *n*-Hexane with Chloro Alkanes

A.K. GUPTA*, C.K. YADAV† and A.S. ANSARI
Department of Chemistry
L.N. Mithila University, Darbhanga-846 008, India

Excess volumes of mixing (V^E) for binary liquid mixtures of *n*-hexane with ethylene dichloride, methylene dichloride, methylene chloride, chloroform and carbon tetrachloride have been measured dilatometrically at temperatures 283.15 K, 293.15 K and 303.15 K. Volume excess of all these mixtures has been found to be positive in sign at entire mole-fraction range. The temperature coefficients $\frac{dV^E}{dT}$ for equimolal mixtures have been found to be positive.

INTRODUCTION

In continuation with our earlier work[1] on measurement of volume excess of mixing of diethyl ether with toluene and xylenes, the present paper describes the measurement and data of V^E for binary liquid mixtures of *n*-hexane with carbon tetrachloride, chloroform, methylene chloride and ethylene-dichloride. Contrary to the negative sign of V^E for the mixtures reported earlier,[1] we observe positive sign at all the temperatures 283.15 K, 293.15 K and 303.15 K. However, the temperature coefficients $\frac{dV^E}{dT}$ for equimolal mixtures were found to be positive as in the former case.[1] The positive sign of V^E for the present mixture is in conformity with the positive sign of the same for *n*-pentane with bromobenzene, xylenes etc. reported by Mahl *et al*[2]. The present work also describes how regular changes in the number of chlorine atoms and their positions in alkanes with same number of chlorine atoms affect the magnitude of volume excess of mixing.

EXPERIMENTAL

n-Hexane (AR, E. Merck), carbon tetrachloride (AR–BDH), chloroform (AR, Glaxo), methylene chloride (AR, Glaxo) and ethylene dichloride (AR, E. Merck) were used after further purification followed by fractional distillation thrice and drying by standard procedures.[3, 4] The purities of these liquides were checked by

---

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

measuring their densities at 303.15 K. The results agreed well with those in literature.[5, 6]

The excess volumes (V^E) of binary liquid mixtures were determined using the dilatometer used by several other authors.[7, 8] The description of experimental procedure has already been given elsewhere.[1] All the measurements were carried out at entire mole fraction range at temperatures 283.15 K, 293.15 K and 303.15 K respectively by the use of themostat regulated to better than ±0.002 K.

RESULTS AND DISCUSSION

Excess volumes of four binary liquid mixtures of *n*-hexane + carbon tetrachloride + chloroform + methylene chloride and + ethylene dichloride for a number of mole-fractions at 283.15 K, 293.15 K and 303.15 K have been presented in Table-1.

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

where *r* is the radius of capillary tube and Δh is the change in mercury levels in capillary, on mixing, of dilatometer, ($n_1 + n_2$) is the total number of moles in the mixture. The values of V^E were fitted to the Redlich-Kister polynomial equation

$$V^E = X_1X_2 \sum_{i=0}^{m} A_i(X_1 - X_2)^i \quad (2)$$

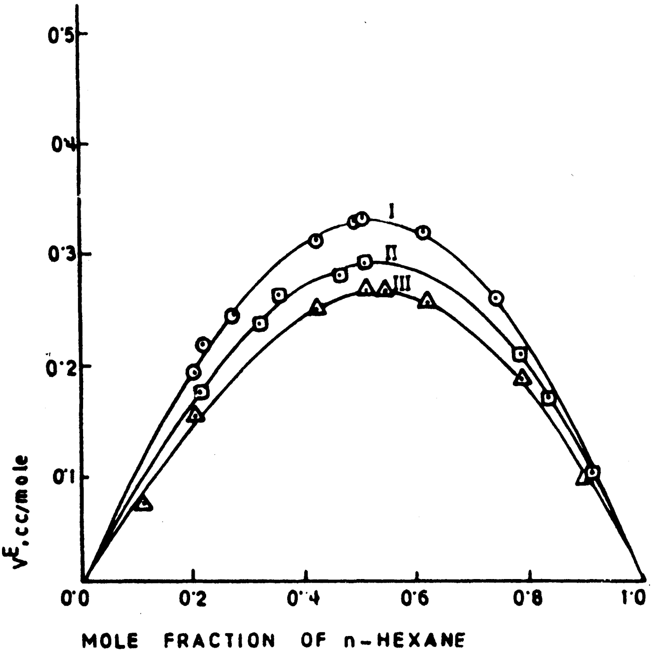

Fig. 1. Excess Volumes of Mixing for *n*-Hexane + Chloroform
Experimental points: I = ○ at 303.15 K, II = ▢ at 293.15 K
III = △ at 283.15
——— Curves calculated from the equation (Table-2)

where X_1 and X_2 are mole fractions of first component (n-hexane) and second component (carbon tetrachloride, chloroform, methylene chloride or ethylene chloride) respectively. The coefficients A_i (A_0, A_1 and A_2 only) of equation (2) have been obtained by the method of least squares and the standard deviation σV^E are calculated from equation

$$\sigma V^E = \left[\Sigma \frac{(V_{obs} - V_{cal})^2}{n - m} \right]^{1/2} \tag{3}$$

where 'n' and 'm' represent the number of experimental points and the number of coefficients used in equation (2) (we have chosen only three coefficients A_0, A_1 and A_2). A_0, A_1 and A_2 along with V^E have been enlisted in Table-2. Temperature dependant V^E equations of the type

$$V^E = X_1X_2[(a_0 + b_0T) + (a_1 + b_1T)(X_1 - X_2) + (a_2 + b_2T)(X_1 - X_2)^2] \tag{4}$$

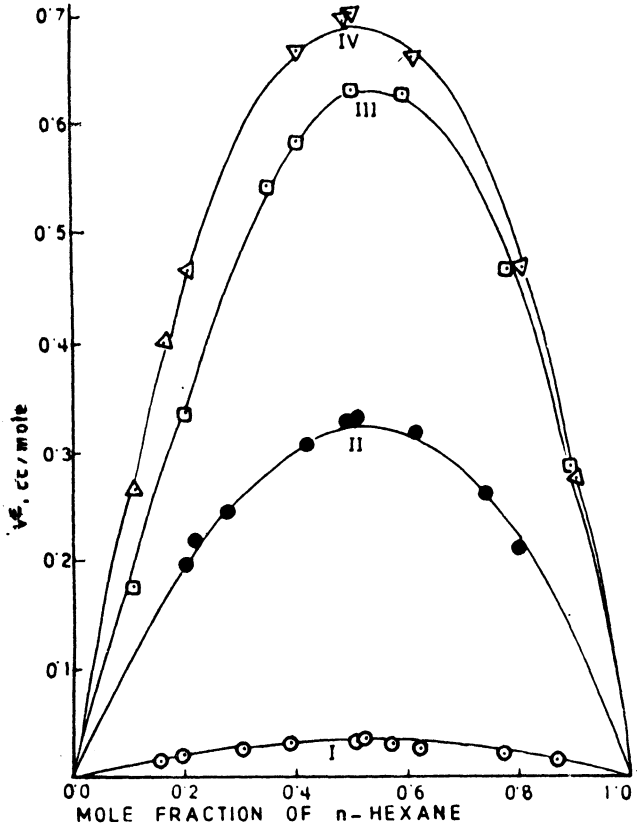

Fig. 2. Excess Volumes of Mixing for

I. n-Hexane + carbon tetrachloride, Experimental point = ⊙
II. n-Hexane + chloroform, Experimental point = ●
III. n-Hexane + methylene chloride, Experimental point = ▣
IV. n-Hexane + ethylene chloride, Experimental point = ▲
——— Curves calculated from the equation (Table 2 at 303.15 k)

for present binary mixtures have also been recorded in Table-3. The last column includes dV^E/dT for equimolal binary mixtures.

It can be seen from Table-1 that excess volume increases with increasing mole-fraction of *n*-hexane till the maximum value is attained and then goes on decreasing with increasing mole fraction at all the temperatures (283.15 K, 293.15 K and 303.15 K) for all of the four binary mixtures under the present investigation. This trend is opposite to the results shown for binary mixtures of diethyl ether and toluene as well as xylenes.[1] However, this shows conformity with the results shown by binary mixtures of *n*-pentane with others.[2] The positive value of temperature coefficient (dV^E/dT) for equimolar mixtures in this case shows the decreasing trend of specific interaction and breaking of associated structures of equimolal mixtures by the rise of temperature. The variation of V^E of *n*-hexane + chloroform as representative of other three binary mixtures, with temperatures mentioned, has been shown by Fig.1. The dependence of V^E on mole fraction (X_1) is almost symmetrical at all the three temperatures. A slight asymmetry in the curves (Fig. 1 and 2) may be related to the molecular correlation of orientation restricted by dipole-dipole and dipole-induced dipole interactions.[9] The positive values of V^E for these mixtures indicate the dominance of dispersive forces over specific interactions.

TABLE-1

EXPERIMENTAL EXCESS VOLUMES (V^E) AT TEMPERATURES (T) FOR MOLE FRACTION X_1 OF n-HEXANE

X_1	V^E (cc mol^{-1})	X_2	V^E (cc mol^{-1})
(X_1 *n*-hexane + X_2 ethylene dichloride at T = 283.15 K)			
0.1126	0.122	0.2081	0.260
0.4043	0.457	0.5086	0.520
0.6188	0.504	0.7762	0.382
0.8998	0.208	—	—
(X_1 *n*-hexane + X_2 ethylene dichloride at T = 293.15 K)			
0.1586	0.225	0.2953	0.420
0.5066	0.604	0.5429	0.590
0.5965	0.583	0.7957	0.416
0.8694	0.310	0.8975	0.241
(X_1 *n*-hexane + X_2 ethylene dichloride at T = 303.15 K)			
0.1141	0.176	0.2055	0.338
0.3526	0.540	0.4021	0.581
0.5051	0.632	0.5976	0.627
0.7837	0.467	0.8896	0.288

(X_1 *n*-hexane + X_2 methylene chloride at T = 283.15 K)

X_1	V^E (cc mol^{-1})	X_2	V^E (cc mol^{-1})
0.1671	0.310	0.2105	0.344
0.3421	0.462	0.4108	0.501
0.4935	0.520	0.5109	0.526
0.6032	0.489	0.8776	0.174
(X_1 *n*-hexane + X_2 methylene chloride at T = 293.15 K)			
0.1631	0.323	0.2235	0.395
0.3396	0.547	0.4888	0.636
0.4963	0.633	0.5143	0.630
0.5628	0.608	0.8011	0.390
0.8746	0.259	–	–
(X_1 *n*-hexane + X_2 methylene chloride at T = 303.15 K)			
0.1147	0.268	0.1628	0.401
0.1984	0.466	0.4058	0.665
0.4963	0.697	0.5029	0.701
0.6128	0.662	0.8038	0.472
0.8989	0.282		
(X_1 *n*-hexane + X_2 chloroform at T = 283.15 K)			
0.1148	0.078	0.2053	0.154
0.4238	0.251	0.5121	0.270
0.5396	0.267	0.6146	0.255
0.7797	0.191	0.9101	0.101
(X_1 *n*-hexane + X_2 chloroform at T = 293.15 K)			
0.2085	0.176	0.3182	0.236
0.3508	0.262	0.4683	0.276
0.4983	0.290	0.5027	0.293
0.5165	0.292	0.7917	0.210
0.8291	0.169	–	–
(X_1 *n*-hexane + X_2chloroform at T = 303.15 K)			
0.2055	0.191	0.2204	0.223
0.2768	0.246	0.4203	0.313
0.4968	0.330	0.5038	0.330
0.6151	0.320	0.7444	0.260
0.8021	0.211	–	–
(X_1 *n*-hexane + X_2 carbon tetrachloride at T = 283.15 K)			
0.1131	0.008	0.2036	0.014
0.3531	0.023	0.3961	0.024
0.4827	0.025	0.5022	0.025
0.6037	0.024	0.7484	0.020
0.7972	0.015	0.8815	0.009

(X_1 *n*-hexane + X_2 carbon tetrachloride at T = 293.15 K)

X_1	V^E (cc mol^{-1})	X_2	V^E (cc mol^{-1})
0.0882	0.008	0.2024	0.016
0.3946	0.029	0.4686	0.029
0.5161	0.029	0.5414	0.029
0.6327	0.028	0.8013	0.018
0.8275	0.018	0.8915	0.009
(X_1 *n*-hexane + X_2 carbon tetrachloride at T = 303.15 K)			
0.1556	0.015	0.2057	0.020
0.3033	0.028	0.3917	0.032
0.5103	0.034	0.5724	0.032
0.6185	0.031	0.7744	0.021
0.8682	0.017	—	—

TABLE-2
VALUES OF CONSTANTS A_0, A_1 and A_2 OF BINARY MIXTURES AND STANDARD DEVIATION σV^E AT TEMPEATURE T (K)

Binary mixtures	T (K)	A_0	A_1	A_2	σV^E/cc mol^{-1}
n-Hexane + Ethylene dichloride	283.15	+ 2.0636	+ 0.6016	− 0.4452	0.0094
	293.15	+ 2.3086	+ 0.6106	− 0.3732	0.0148
	303.15	+ 2.5536	+ 0.6196	− 0.3012	0.0106
n-Hexane + Methylene chloride	283.15	+ 2.0636	− 0.2112	− 0.4055	0.0142
	293.15	+ 2.4196	+ 0.0088	− 0.1225	0.0373
	303.15	+ 2.7756	+ 0.2288	+ 0.1605	0.0073
n-Hexane + Chloroform	283.15	+ 1.0618	+ 0.1860	− 0.1697	0.0067
	293.15	+ 1.1841	+ 0.1521	− 0.1073	0.0080
	303.15	+ 1.3064	+ 0.1182	− 0.0448	0.0065
n-Hexane + Carbon tetrachloride	283.15	+ 0.1003	+ 0.0073	− 0.0043	0.0001
	293.15	+ 0.1203	+ 0.0043	− 0.0133	0.0008
	303.15	+ 0.1373	+ 0.0013	− 0.0223	0.0010

n-Hexane and carbon tetrachloride are nonpolar molecules. On the other hand, chloroform, methylene chloride and ethylene dichloride are polar molecules. (Dipole moments are 1.15 D, 1.59 D and 1.86 D respectively). The strength of dipole-dipole as well as dipole-induced dipole interactions varies in same order. The positive values of V^E suggest that expansion caused by breaking of associated structures in pure liquid molecules due to dipole-dipole interactions exceeds the contraction due to specific interactions between unlike molecules (dipole-induced dipole interaction).

TABLE-3

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

Binary Mixtures	Equations fitting the expt data	dV^E/dT
n-Hexane + Ethylene dichloride	$\frac{V^E}{cc\ mol^{-1}} = X_1X_2[(-4.8735 + 0.0245T)$ $+ (0.3468 + 0.0009T)(X_1 - X_2)$ $+ (-2.4838 + 0.0072T)(X_1 - X_2)^2]$	0.0061
n-Hexane + Methylene chloride	$\frac{V^E}{cc\ mol^{-1}} = X_1X_2[(-8.0165 + 0.0356T)$ $+ (-6.4405 + 0.0220T)(X_1 - X_2)$ $+ (-3.4186 + 0.0283T)(X_1 - X_2)^2]$	0.0089
n-Hexane + Chloroform	$\frac{V^E}{cc\ mol^{-1}} = X_1X_2[(-2.4015 + 0.0123T)$ $+ (1.1458 + 0.0033T)(X_1 - X_2)$ $+ (1.9365 + 0.0362T)(X_1 - X_2)^2]$	0.0030
n-Hexane + Carbon tetrachloride	$\frac{V^E}{cc\ mol^{-1}} = X_1X_2[(-3.3780 + 0.0017T)$ $+ (0.0922 + 0.0003T)(X_1 - X_2)$ $+ (0.2505 + 0.0009T)(X_1 - X_2)^2]$	0.0004

The order of variation in the values of V^E for equimolal mixtures at the temperatures 283.15 K, 293.15 K and 303.15 K follows as

V^E: n-hexane + ethylene dichloride > + methylene chloride >
+ chloroform > + carbon tetrachloride

This is evident from Fig. 2 that the above holds equally good at all compositions of binary mixtures. The comparative plot of V^E (Fig. 2) for binary mixtures shows that V^E for n-hexane + carbon tetrachloride is very small in comparison to other binaries. This indicates the absence of dipolar structures in pure carbon tetrachloride molecules. Hence, the expansion is not due to breaking of dipolar structures of carbon tetrachloride as it occurs in the case of ethylene dichloride, nethylene chloride and chloroform by the additions of nonpolar solvent (n-hexane).

The variation of V^E may be correlated with the number of chlorine atoms per carbon atom and dipole moments of second component of binary mixtures.

Number of Cl-atoms per carbon atom: $C_2H_4Cl_2 < CH_2Cl_2 < CH_3Cl_3 < CCl_4$
Dipole moments: $C_2H_4Cl_2 > CH_2Cl_2 > CHCl_3 < CCl_4$
Excess volume: $\underset{\text{(n-hexane)}}{C_6H_{14}} + C_2H_4Cl_2 > + CH_2Cl_2 > + CHCl_3 > + CCl_4$

ACKNOWLEDGEMENT

We are thankful to Prof. R.B. Yadav, Ex-Vice-Chancellor, B.N.M. University, Madhepura, presently Prof. and Head of the Department of Chemistry, C.M.Sc.

College, Darbhanga and Dean of Science L.N. Mithila University, Darbhanga for his valuable suggestions and guidance.

REFERENCES

1. A.K. Gupta and C.K. Yadav, *Asian. J. Chem.*, **9**, 112 (1997).
2. B.S. Mahl, R.K. Nigam, S.L. Chopra and P.P. Singh, *J. Chem. Thermodynamics*, **3**, 363 (1971).
3. K.A. Klain, *J. Ass. Office. Agr. Chem*, **32**, 349 (1949).
4. Wey Gand, Hilgetag, Preparative Organic Chemistry, John Wiley and Sons, p. 1096 (1956).
5. J. Timmermans, Physico-Chemical Constants of Pure Organic Compounds, Elsevier Publishing Company, pp. 11, 97, 180, 184 (1965).
6. R.P. Rastogi, Jagan Nath and R.B. Yadav, *Indian J. Chem.*, **9**, 541 (1970).
7. ________, *Indian. J. Chem.*, **9**, 45 (1971).
8. W.A. Duncan, J.P. Sheridan and P.L. Swinton, *Trans. Faraday Soc.*, **62**, 1090 (1966).
9. S.L. Oswal and N.B. Patel, *J. Chem. Eng. Data*, **40**, 845 (1995).

(*Received:* 28 November 1996; *Accepted:* 3 January 1997) AJC-1236