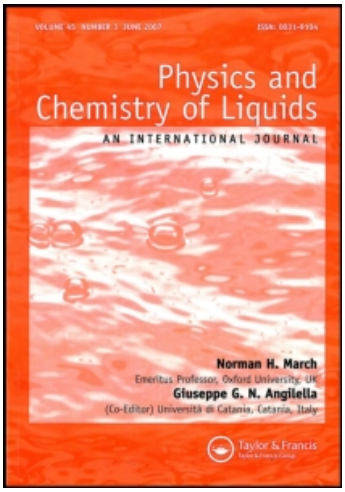

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Excess Enthalpies of Binary Mixtures of 2-Propen-1-Ol with Chloroalkanes and Chloroalkenes at 298.15 K

R. Vijaya Kumar[a]; M. Anand Rao[a]; M. Venkateshwara Rao[b]; A. Rajiah[c]
[a] Department of Chemistry, Osmania University, Hyderabad, India [b] College of Technology, Osmania University, Hyderabad, India [c] Indian Institute of Chemical Technology, Hyderabad, India

To cite this Article Kumar, R. Vijaya , Rao, M. Anand , Rao, M. Venkateshwara and Rajiah, A.(1996) 'Excess Enthalpies of Binary Mixtures of 2-Propen-1-Ol with Chloroalkanes and Chloroalkenes at 298.15 K', Physics and Chemistry of Liquids, 31: 1, 33 — 37
To link to this Article: DOI: 10.1080/00319109608029555
URL: http://dx.doi.org/10.1080/00319109608029555

Phys. Chem. Liq., 1996, Vol. 31, pp. 33–37
Reprints available directly from the publisher
Photocopying permitted by license only

EXCESS ENTHALPIES OF BINARY MIXTURES OF 2-PROPEN-1-OL WITH CHLOROALKANES AND CHLOROALKENES AT 298.15 K

R. VIJAYA KUMAR[1], M. ANAND RAO*[,1], M. VENKATESHWARA RAO[2] and A. RAJIAH[3]

[1]*Department of Chemistry, Osmania University, Hyderabad-500 007, India*
[2]*College of Technology, Osmania University, Hyderabad-500 007, India*
[3]*Indian Institute of Chemical Technology, Hyderabad-500 007, India*

(Received 8 June 1995)

Excess molar enthalpies of binary mixtures of 2-propen-1-ol with 1,2-dichloroethane, 1,1,1,-trichloroethane, 1,1,2,2-tetrachloroethane, trichloroethylene and tetrachloroethylene have been measured at 298.15 K using a 1451 Parr model solution calorimeter. The excess enthalpy values are positive in all the systems over the entire range of mole fraction except for the system involving 1,1,2,2-tetrachloroethane. All the excess enthalpy curves are found to be S shaped. Comments on the effect of intramolecular interactions on the intermolecular interactions have been made on the basis of the experimental results.

KEY WORDS: Excess enthalpy, 2-propyn-1-ol, chloroalkanes and chloroalkenes.

1 INTRODUCTION

The magnitude of the excess enthalpies for non ideal solutions can be quite significant and can provide a direct measure of molecular interactions. The thermodynamic properties of binary mixtures containing polar and self associated components exhibit significant deviation from ideality, arising not only from the difference in size and shape but also from possible hydrogen bonding interactions betwen unlike molecules. A careful literature survey has shown that excess molar enthalpies ΔH_m^E of binary mixtures containing haloalkanes, haloalkenes and chlorobenzene with *n*-propanol have been reported[1–5], while excess enthalpies of 2-propen-1-ol with chloroalkanes and chloroalkenes have not been studied. Excess enthalpies for the binary systems of 2-propen-1-ol + 1,2-dichloroethane, + 1,1,1-trichloroethane, + 1,1,2,2,-tetrachloroethane, + trichloroethylene, + tetrachloroethylene at 298.15 K, are reported in this paper.

2 EXPERIMENTAL

The chemicals used were purified by the standard methods described by Riddick, Bunger, and Sakano[6]. 2-propen-1-ol (Fluka AR grade) was fractionally distilled twice,

*Author to whom correspondence should be addressed.

and the middle fraction of the second distillation was collected. 1,2-dichloroethane (Merck AR grade) was washed with dilute potassium hydroxide solution, dried over anhydrous calcium-chloride, and fractionally distilled. 1,1,1-trichloroethane (Merck AR grade) was washed with concentrated hydrochloric acid and then with 10% sodium chloride solution, dried over solid calcium chloride, and finally fractionally distilled twice, and the middle fraction of the second distillation was collected. 1,1,2,2-tetrachloroethane (Merck AR grade) was shaken with concentrated sulfuric acid for about 10 min at 80–90°C. The operation was repeated until the acid developed no more color. It was then washed with water, steam distilled, dried over potassium carbonate, and finally fractionated. Spectral grade trichloroethylene and tetrachloroethylene (S.D. Fine Chemicals Pvt. Ltd, Boisar India) were fractionally distilled twice and the middle fraction of the second distillation was collected.

The purity of the samples has been checked with those reported in the literature by comparing the measured densities and refractive indices of the purified samples by means of a pycnometer and Abbe's refractometer, thermostated to the required temperature. The measured values were in agreement with the literature data[6] within 0.1% as shown in Table 1. Excess enthalpies were measured using a Parr 1451 solution calorimeter. Details of the calorimeter and experimental procedure were described earlier[7].

3 RESULTS AND DISCUSSION

The measured molar excess enthalpies ΔH_m^E of 2-propen-1-ol + 1,2-dichloroethane, + 1,1,1-trichloroethane, + 1,1,2,2-tetrachloroethane, + trichloroethylene, + tetrachloroethylene at 298. 15 K are given in Table 2 and shown in Figure 1. The results were fitted to:

$$\Delta H_m^E/(J \cdot mol^{-1}) = (1 - x) \times \sum h_j (2x - 1)^j \quad (1)$$

by the method of least squares. Values of coefficients h_j and the standard deviation $\sigma(\Delta H_m^E)(\%)$ representing the fit of each set of results are given in Table 3. For the

Table 1 Comparison of densities and refractive indices at 298. 15 K with literature data.

Component	$\rho/g - Cm^{-3}$		n_D	
	Lit[5]	*Expt*	*Lit[5]*	*Expt*
2-propen-1-ol	0.84209	0.84210	1.40900	1.40903#
1,2-dichloroethane	1.24637	1.24682	1.44210	1.44216
1,1,1-trichloroethane	1.32990	1.32950	1.43590	1.43588
1,1,2,2-tetrachloroethane	1.58666	1.58628	1.49140	1.49187
trichloroethylene	1.61432	1.61418	1.50320	1.50318
tetrachloroethylene	1.66220	1.66185	1.41300	1.41370

at 303.15 K

systems studied, the excess enthalpies at 298. 15K are endothermic except for those of 1,1,2,2-tetrachloroethane. Similar trends were observed for the benzyl alcohol with the same chloroalkanes and chloroalkenes at 298. 15K[7]. Excess enthalpies are influenced by two opposing effects viz; 1) absorption of heat due to depolymerisation of self associated alcohols i.e., dissociation of self associated alcohols by chloroalkanes and chloroalkenes resulting in the reduction in dipole-dipole interactions between like molecules, and 2) liberation of heat as a result of possible hydrogen bonding interaction between halogenated group of alkane, and hydroxyl function of the alcohol. The actual

Table 2 Mole fraction of 2-propen-1-ol (x) and molar excess enthalpy ΔH_m^E for mixtures of 2-propen-1-ol with chloroalkanes and chloroalkenes at 298.15 K.

(x)	$\Delta H_m^E/(J \cdot mol^{-1})$	(x)	$\Delta H_m^E/(J \cdot mol^{-1})$
(x) 2-propen-1-ol + (1 − x) 1,2-dichloroethane		(x) 2-propen-1-ol + (1 − x) 1,1,1-trichloroethylene	
0.0507	536.6	0.0670	587.4
0.1381	979.4	0.1444	765.0
0.1986	1106.5	0.2111	835.2
0.2560	1157.4	0.2730	855.6
0.3542	1197.6	0.3700	843.9
0.4742	1125.0	0.4205	831.6
0.5471	1033.6	0.5594	791.9
0.6221	1118.9	0.6358	685.9
0.6980	942.6	0.7038	582.5
0.7694	742.3	0.7714	470.0
0.8313	545.8	0.8373	339.0
0.9126	286.8	0.9103	182.0
0.9768	69.6	0.9783	39.0
0.0929	543.9	0.0650	427.0
0.1439	669.3	0.1491	560.8
0.2170	741.3	0.2511	567.8
0.2937	729.3	0.3188	543.3
0.3657	664.5	0.3806	504.6
0.4371	543.9	0.4267	468.4
0.5087	422.2	0.5671	443.3
0.5871	273.1	0.6301	369.6
0.6624	126.5	0.6899	288.7
0.8036	−97.8	0.7710	190.3
0.8859	−131.7	0.8452	104.4
0.9145	−123.1	0.9054	46.2
0.9767	−48.1	0.9773	3.9
		0.0872	488.7
		0.1438	553.5
		0.1917	606.3
		0.2812	664.4
		0.3547	681.7
		0.4160	694.6
		0.5613	753.7
		0.6341	702.8
		0.6990	621.1
		0.7683	525.3
		0.8467	386.3
		0.9115	243.3
		0.9701	86.0

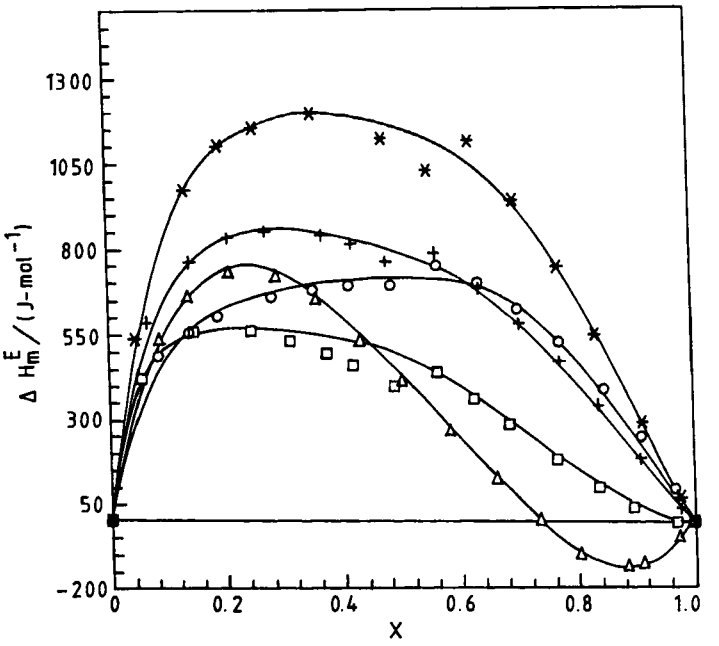

Figure 1 Excess enthalpies ΔH_m^E at 298.15 K of 2-propen-1-ol (x) + $(1-x)$ 1,2-dichloroethane (*), + $(1-x)$ 1,1,1-trichloroethane (+) + $(1-x)$ 1,1,2,2-tetrachloroethane (Δ) + $(1-x)$ trichloroethylene (□) + $(1-x)$ tetrachloroethylene (○).

Table 3 Values of coefficients h_j in equation (1) determined by least squares analysis, and percentage standard deviation $\sigma(\Delta H_m^E)$ in the mixtures of 2-propen-1-ol (x) with chloroalkanes $(1-x)$ and chloroalkenes $(1-x)$ at 298.15 K.

system	h_0	h_1	h_2	h_3	h_4	h_5	$\sigma(\Delta H^E_m)$ / (J·mol^{-1})
$(1-x)ClH_2CCH_2Cl$ + $(x)H_2C{=}CH{-}CH_2OH$	4556.98	−710.85	2264.52	−4510.32	1255.04	--	4.09
$(1-x)Cl_3CCH_3$ + $(x)H_2C{=}CH{-}CH_2OH$	3307.75	−1206.59	−124.37	−1171.93	4503.10	−3694.10	2.04
$(1-x)Cl_2HCCHCl_2$ + $(x)H_2C{=}CH{-}CH_2OH$	1774.74	−3748.16	181.32	−1400.58	1307.92	−446.25	2.10
$(1-x)Cl_2C{=}CHCl$ + $(x)H_2C{=}CH{-}CH_2OH$	1884.50	−1073.70	−235.79	−2340.70	3614.27	−1811.26	3.72
$(1-x)Cl_2C{=}CCl_2$ + $(x)H_2C{=}CH{-}CH_2OH$	2997.22	120.61	−360.35	−1341.36	3858.75	−2316.14	2.62

value of ΔH_m^E would depend upon the strength of two opposing effects. The positive experimental enthalpies suggests that the first effect is stronger than the second for all the systems, except the 2-propen-1-ol + 1,1,2,2-tetrachloro- ethane system. The first effect is assumed to be stronger upto 0.7 mole fraction of 2-propen-1-ol and second effect is stronger for alcohol rich range.

For the systems of 2-propen-1-ol with chloroalkanes and chloroalkenes, the excess enthalpies are found to be in the following order:
1,2-dichloroethane(1197.6) > 1,1,1-trichloroethane(855.6) > tetrachloroethylene (753.7) > trichloroethylene (567) > 1,1,2,2-tetrachloroethane (741.3) and (−131.7).

Acknowledgement

The authors wish to thank Dr. D. H. L. Prasad, Scientist, Indian Institute of Chemical Technology, for his helpful suggestions.

References

1. S. K. Chaudari and S. S. Katti, *Thermochim. Acta*, **99**, 158 (1990).
2. J. L. Zuita, M. L. G. Desocis, M. A. Postigo and M. Katz, *J. Solution Chem.*, **16**, 163 (1987).
3. I. Nagata and K. Tamura, *J. Chem. Thermodyn*, **20**, 87 (1988).
4. K. Rambabu, P. Venkateshwarlu, G. K. Raman and Y. V. L. Ravi Kumar, *Phys. Chem. Liq.*, **21**, 97 (1990).
5. Y. X. Wang, J. P. Chao and M. Dai., *Thermochim Acta*, **161**, 169 (1990).
6. J. A. Riddick; W. B. Bunger and K. Sakano., Organic Solvents Physical Properties and Methods of Purification, Vol. 2. 4th ed; Wiley Interscience; New York, 1986.
7. R. Vijaya kumar, M. Anand Rao, M. Venkateshwar Rao and A. Rajiah *J. Chem. Eng. Data*, **40**, 99 (1995).