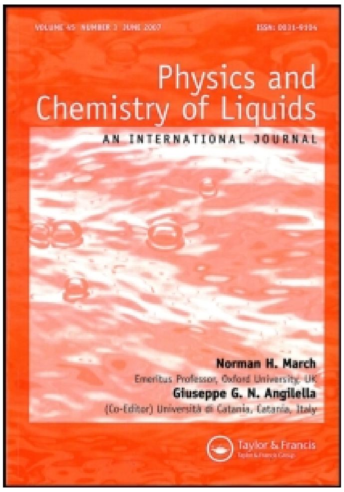

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J. D. Pandey[a]; R. Dey[a]; R. Verma[a]
[a] Department of Chemistry, University of Allahabad, Allahabad, India

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THERMODYNAMIC PROPERTIES OF MULTICOMPONENT LIQUID MIXTURES

J.D. PANDEY*, R. DEY and R. VERMA

Department of Chemistry, University of Allahabad, Allahabad-211 002, India

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Considering a ternary liquid mixture to be made up of three binary mixtures, by means of cell model using Sutherland type potential function for pair interaction between molecules, a statistical theory for binary liquid mixtures has been extended for ternary systems. In the light of above extension, excess volume (V^E), excess energy (E^E) and excess entropy (TS^E) have been computed for three binary (benzene + cyclohexane, benzene + chlorobenzene and cyclohexane + chlorobenzene) and the resultant ternary system (benzene + cyclohexane + chlorobenzene) at 298.15 K. All the above mentioned excess properties have been computed from the data of ultrasonic velocity and density only.

Keywords: Excess volume; Excess energy; Excess entropy; Ternary mixture

INTRODUCTION

The chemical industry has long since recognized the importance of thermodynamic and physical properties in design calculations involving chemical separations, fluid flow and heat transfer. However, even with today's sophisticated instrumentation, experimental measurements of thermodynamic properties become progressively more and more difficult and time consuming with each additional component beyond binary mixtures. To address this problem, engineers have turned to predictive methods as a means to generate desired quantities. For many practical purposes, it is necessary to predict the excess properties of a multicomponent liquid mixture from the properties of pure components and from the data containing only variables such as density, velocity of sound etc. The study of thermodynamic functions such as excess volume (V^E), excess energy (E^E), excess viscosity (η^E) and various other thermodynamic functions are useful in understanding the nature of intermolecular interactions between component molecules [1–3]. Due to scarcity of ternary liquid mixtures data [4–6], here an attempt has been made to extend a statistical mechanical theory proposed by Arakawa [7] to ternary liquid mixture, assuming the ternary system is made up of three binary liquid mixtures. Thus many equations have been derived for predicting the thermodynamic excess properties from binary and pure component experimental data [1–5].

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*Corresponding author.

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The ternary system undertaken for the present investigation is benzene + cyclohexane + chlorobenzene. For the sake of completeness the excess properties of individual binary liquid mixtures have also been computed. Extension to the ternary system was made using the cell model in combination with the radial distribution function, where the interaction potential between molecules is assumed to be of Sutherland type.

It is indicated that this approach particularly for ternary systems may prove to be a valuable tool in determining excess properties as (i) the results are found to be in good agreement with literature and (ii) after incorporating Schaaffs equation [8] only the ultrasonic velocity, density data is needed for the prediction of excess functions of both binary and ternary liquid mixtures.

THEORETICAL

The whole approach assumes that the molecules are rigid spheres and the potential of interaction between two molecules is a function of intermolecular separation. The shape of the average potential function of mutual interaction is nearly like a square well. Making use of the partition function and the equation of state, Arakawa *et al* [7] derived the following excess functions for binary liquid mixtures;

Excess energy

$$E^E = 3RT\left\{\left(\frac{x_A\upsilon_A^0}{\upsilon_A^0-\beta r_{AA}^{*3}}+\frac{x_B\upsilon_B^0}{\upsilon_B^0-\beta r_{BB}^{*3}}\right)-\frac{\upsilon}{\upsilon-\beta(x_Ar_A^{*3}+x_Br_B^{*3})}\right\} \tag{1}$$

For the excess volume,

$$\frac{V^E}{N}=\beta\left(x_Ar_A^{*3}+x_Br_B^{*3}\right)\left(\frac{K-E_E}{K-E_E-3RT}\right)-\overline{\upsilon_0} \tag{2}$$

Here

$$K=3RT\left\{\left(\frac{x_A\upsilon_A^0}{\upsilon_A^0-\beta r_{AA}^{*3}}\right)+\left(\frac{x_B\upsilon_B^o}{\upsilon_B^0-\beta r_{BB}^{*3}}\right)\right\}\quad\text{and}\quad\overline{\upsilon_0}=x_A\upsilon_A^0+x_B\upsilon_B^0$$

For excess entropy,

$$TS^E=3RT\left[x_A\ln\left\{\frac{\upsilon_A^0-\beta r_{AA}^{*3}}{\upsilon-\beta(x_Ar_A^{*3})}\left(\frac{r_A^*}{r_{AA}^*}\right)^2\right\}+x_B\ln\left\{\frac{\upsilon_B^0-\beta r_{BB}^{*}}{\upsilon-\beta(x_Ar_A^{*3}+x_Br_B^{*3})}\left(\frac{r_B^*}{r_{BB}^*}\right)^2\right\}\right] \tag{3}$$

In the above equations, R is gas constant, T the absolute temperature, x_A, x_B the mole fractions of A and B respectively, υ_A^0, υ_B^0 the volume per molecule for the mixture,

β the common packing parameter, r^*_A, r^*_B the collision diameter of the molecule within each cell and r^*_{AA}, r^*_{BB} the diameter of each species in pure state.

For the computation of the above mentioned excess functions, Schaaffs equation [8] for sound velocity (υ),

$$U^2 = \gamma RT\left[\frac{(1/3)M}{(M-\rho b)^2} - \frac{2}{(M-\rho b)}\right] \tag{4}$$

has been employed for the calculation of the molecular diameter of pure liquids r^*_{AA} etc.

Hence, M is molecular weight, γ the ratio of specific heats and b is van der Waals constant given by $b=(16/3)\pi r^{*3}_{AA}N$, r^*_{AA} being the molecular radius for organic liquid, N is Avogadro's number and ρ the density.

The molecular diameters are related to the collision diameter of the molecule within each cell by formulae,

$$r^*_A = x_A r^*_{AA} + x_B r^*_{AB}$$

$$r^*_B = x_A r^*_{AB} + x_B r^*_{BB} \quad \text{and}$$

$$r^*_{AB} = \frac{1}{2}(r^*_{AA} + r^*_{BB})$$

The packing parameter is given by the relation [7],

$$\beta r^{*3}_{AA} = \upsilon^0_A\left(\frac{1+\alpha_A T}{1+(4/3)\alpha_A T}\right)^3$$

where α_A is thermal expansion coefficient of component A, computed by employing the recently proposed relationship [9,14] $\alpha=(75.6\times10^{-3})/(T^{-1/9}U^{1/2}\rho^{1/3})\,\mathrm{deg}^{-1}$, where all the terms have their usual meaning. U, ρ and T are expressed respectively in ms^{-1}, $\mathrm{g\,cm}^{-3}$ and K. For the ternary system, the equations have been extended and the various functions are given by,

$$E^E = E - x_A E^0_A - x_B E^0_B - x_C E^0_C$$

$$S^E = S - x_A S^0_A - x_B S^0_B - x_C S^0_C - \Delta S^{\mathrm{id}}_{\mathrm{mix}} \quad \text{and}$$

$$V^E = V - x_A V^0_A - x_B V^0_B - x_C V^0_C$$

Furthermore, the collision diameters of the molecule within each cell for the ternary system have been evaluated by making use of the following equations:

$$r^*_A = x_A r^*_{AA} + x_B r^*_{AB} + x_C r^*_{AC}$$

$$r^*_B = x_B r^*_{BB} + x_A r^*_{AB} + x_C r^*_{BC}$$

$$r^*_C = x_C r^*_{CC} + x_A r^*_{AC} + x_B r^*_{BC}$$

RESULTS AND DISCUSSION

In the present investigation, a statistical theory given for binary liquid mixtures has been extended for ternary systems and it has been tested by computation of excess energy E^E, excess volume V^E and TS^E for the binary liquid mixtures viz; benzene + cyclohexane, benzene + chlorobenzene, cyclohexane + chlorobenzene, and the resultant ternary systems, benzene + cyclohexane + chlorobenzene, at 298.15 K. The aim in choosing the three binary systems lies in the diversified nature of the compounds undertaken for the present investigation and to carry out a comparative study thereof. The required data containing speeds of sound and density have been taken from the literature [10]. The values of the excess parameters have been listed in the Tables II–V and for some binary systems are also illustrated graphically.

Using the Prigogine–Flory [11,12] theory one can rationalize the signs and magnitudes of the excess functions obtained. Especially for E^E there are two contributions to excess energies, (more specifically enthalpies) each of which has a counter part in V^E, viz., (1) the positive interactional terms due to any dissimilarity in dispersion force fields surrounding the molecules of the two liquids of dissimilar chemical nature and (2) negative term due to dissimilarity of the free volume of liquids. It is seen that these two terms are not sufficient to explain why large positive values of H^E are obtained when two liquids of similar chemical nature and free volumes are mixed. This is explained on the grounds of order changes which occur on addition of a second liquid, which though similar chemically has little orientational order. Liquids like benzene, bear quadrupole moments which create structure, on addition of cyclohexane order is destroyed, leading to large positive values of H^E.

TABLE I Molecular parameters of pure liquids at 298.15 K

	$M.Wt$ (gm)	U (ms^{-1})	ρ (gm/cc)	α (deg^{-1})	r^*_{AA} (cm^{-1})	ΔH^w (cal/mol)
c-C_6H_{12}	84.16	1252	0.774	0.00122	2.16E-08	7862.31
C_6H_6	78.14	1295	0.874	0.00123	2.02E-08	7892.84
C_6H_5Cl	113.64	1268	1.008	0.00109	2.12E-08	8495.99

TABLE II Excess thermodynamic quantities for the binary system $C_6H_6 + C_6H_{12}$ at 298.15 K

x_1	x_2	U(ms^{-1})	ρ(gm/cc)	α (deg^{-1})	b	v_a (cc/mol)	E^E (cal/mol)	V^E (cc/mol)	TS^E (cal/mol)
0.080	0.920	1251	0.779	0.0012	99.29	107.22	66.57	0.184	23.11
0.127	0.873	1250	0.782	0.0012	98.44	106.38	99.85	0.272	36.40
0.170	0.830	1249	0.785	0.0012	97.69	105.65	131.04	0.360	47.95
0.284	0.716	1249	0.794	0.0012	95.65	103.62	195.60	0.530	75.88
0.382	0.618	1250	0.803	0.0012	93.91	101.82	231.45	0.614	94.60
0.430	0.570	1251	0.807	0.0012	93.06	100.92	243.62	0.640	101.64
0.532	0.468	1255	0.817	0.0012	91.25	98.96	252.01	0.643	110.09
0.667	0.333	1263	0.831	0.0012	88.84	96.27	230.28	0.560	105.79
0.721	0.279	1267	0.836	0.0012	87.87	95.28	242.80	0.615	105.67
0.744	0.256	1270	0.840	0.0012	87.47	94.70	200.67	0.473	94.21
0.751	0.249	1270	0.841	0.0012	87.34	94.56	198.86	0.470	93.15
0.838	0.162	1279	0.852	0.0012	85.78	92.74	148.66	0.340	70.55
0.872	0.128	1282	0.856	0.0012	85.19	92.04	126.00	0.286	59.58
0.905	0.095	1286	0.860	0.0012	84.60	91.34	99.09	0.223	46.79
0.976	0.024	1296	0.870	0.0012	83.34	89.81	27.48	0.059	13.12

TABLE III Excess thermodynamic quantities for the binary system $C_6H_6+C_6H_5Cl$ at 298.15 K

x_1	x_2	$U(\text{ms}^{-1})$	ρ(gm/cc)	α (deg^{-1})	b	v_a(cc/mol)	E^E(cal/mol)	V^E(cc/mol)	TS^E(cal/mol)
0.079	0.921	1269	1.085	0.0011	94.88	100.74	3.46	−0.017	721.32
0.107	0.893	1269	1.079	0.0011	94.51	100.38	3.51	−0.026	863.64
0.166	0.834	1270	1.067	0.0011	93.75	99.65	7.94	−0.028	1078.54
0.222	0.778	1271	1.056	0.0011	93.02	98.94	10.40	−0.034	1212.21
0.273	0.727	1272	1.045	0.0011	92.35	98.31	13.71	−0.033	1288.35
0.348	0.652	1274	1.029	0.0011	91.38	97.37	16.64	−0.035	1339.02
0.379	0.621	1275	1.022	0.0011	90.98	96.99	18.19	−0.034	1342.10
0.462	0.538	1277	1.004	0.0011	89.90	95.97	22.37	−0.026	1306.68
0.513	0.487	1278	0.992	0.0011	89.24	95.33	23.23	−0.024	1256.86
0.598	0.402	1281	0.972	0.0011	88.13	94.28	24.34	−0.017	1131.79
0.645	0.355	1283	0.961	0.0011	87.52	93.70	24.34	−0.012	1043.25
0.742	0.258	1286	0.938	0.0011	86.26	92.49	23.09	−0.002	819.13
0.776	0.224	1288	0.930	0.0011	85.82	92.07	20.42	−0.004	728.95
0.820	0.180	1290	0.919	0.0011	85.24	91.53	18.73	0.001	604.16
0.867	0.133	1292	0.907	0.0012	84.63	90.94	14.57	0.001	459.39
0.904	0.097	1294	0.898	0.0012	84.16	90.49	12.61	0.005	342.21

TABLE IV Excess thermodynamic quantities for the binary system $C_6H_{12}+C_6H_5Cl$ at 298.15 K

x_1	x_2	$U(\text{ms}^{-1})$	ρ(gm/cc)	α (deg^{-1})	b	v_a(cc/mol)	E^E(cal/mol)	V^E(cc/mol)	TS^E(cal/mol)
0.037	0.964	1265	1.088	0.0011	96.08	102.01	9.55	0.018	−711.19
0.100	0.901	1261	1.066	0.0011	96.38	102.47	24.73	0.048	−952.64
0.124	0.876	1260	1.057	0.0011	96.50	102.66	30.95	0.062	−977.30
0.163	0.837	1257	1.044	0.0011	96.69	102.94	41.40	0.087	−980.39
0.204	0.796	1255	1.030	0.0011	96.88	103.25	52.35	0.116	−955.42
0.248	0.752	1253	1.014	0.0011	97.10	103.60	67.95	0.162	−910.29
0.280	0.720	1251	1.003	0.0011	97.25	103.84	77.16	0.190	−869.33
0.326	0.674	1249	0.987	0.0011	97.47	104.19	86.69	0.219	−803.22
0.387	0.613	1247	0.967	0.0011	97.77	104.64	96.77	0.253	−710.92
0.469	0.531	1244	0.940	0.0012	98.16	105.22	102.32	0.275	−584.85
0.534	0.466	1242	0.919	0.0012	98.47	105.67	103.83	0.285	−489.08
0.633	0.367	1242	0.886	0.0012	98.95	106.36	103.32	0.298	−354.95
0.733	0.268	1242	0.855	0.0012	99.43	107.03	94.74	0.287	−239.86
0.789	0.211	1243	0.837	0.0012	99.70	107.38	81.15	0.250	−182.58
0.857	0.143	1245	0.816	0.0012	100.02	107.80	65.65	0.210	−124.74
0.904	0.096	1248	0.802	0.0012	100.25	108.08	48.66	0.159	−89.85

Excess volume on the other hand contains a third contribution called P^* (internal pressure) contribution [13]. This term often dominates V^E particularly when one component is of higher P^*, and lower thermal expansion coefficient, leading to negative V^E, coupled with positive H^E values. Excess volumes can also be discussed in terms of two factors [7],

$$V^E = V^E(\text{size}) + V^E(\text{int})$$

V^E (size) corresponds to the size difference of molecules and the other V^E(int) is associated with the interaction between molecules. The values of V^E(int) be either positive or negative whereas the first term,

$$\begin{aligned} V^E(\text{size}) &< 0 \quad \text{for } r^*_{AA} \neq r^*_{BB} \\ &= 0 \quad \text{for } r^*_{AA} = r^*_{BB} \end{aligned}$$

TABLE V Excess thermodynamic quantities for the ternary system x_1–C_6H_6 + x_2–C_6H_{12} + $(1-x_1-x_2)C_6H_5Cl$ at 298.15 K

x_1	x_2	x_3	$U\,(\mathrm{ms}^{-1})$	ρ (gm/cc)	α (deg^{-1})	b	v_a (cc/mol)	E^E (cal/mol)	V^E (cc/mol)	TS^E (cal/mol)
0.072	0.231	0.698	1255	1.005	0.0011	96.09	102.59	63.20	0.158	16.95
0.071	0.424	0.505	1247	0.939	0.0012	97.03	104.04	145.03	0.286	35.74
0.072	0.525	0.403	1244	0.905	0.0012	97.49	104.76	177.27	0.336	43.30
0.077	0.619	0.304	1243	0.874	0.0012	97.88	105.36	196.72	0.353	47.71
0.077	0.721	0.202	1244	0.841	0.0012	98.38	106.04	202.49	0.325	48.24
0.083	0.804	0.113	1246	0.814	0.0012	98.69	106.51	209.57	0.315	49.67
0.165	0.327	0.508	1252	0.951	0.0012	95.34	102.21	134.02	0.284	35.34
0.105	0.730	0.165	1245	0.832	0.0012	98.05	105.79	217.08	0.365	52.89
0.167	0.718	0.115	1246	0.821	0.0012	97.19	104.99	237.86	0.423	60.13
0.288	0.228	0.484	1258	0.959	0.0011	93.26	99.95	104.11	0.233	29.87
0.293	0.599	0.108	1248	0.830	0.0012	94.98	102.72	263.61	0.534	70.59
0.390	0.130	0.481	1266	0.972	0.0011	91.47	97.90	47.18	0.126	16.75
0.388	0.225	0.388	1261	0.937	0.0012	91.95	98.73	122.05	0.278	35.63
0.392	0.313	0.295	1256	0.905	0.0012	92.31	99.38	176.15	0.384	49.52
0.399	0.402	0.199	1253	0.872	0.0012	92.64	99.99	224.58	0.486	62.37
0.482	0.048	0.470	1274	0.981	0.0011	89.87	96.11	−2.78	0.054	5.24
0.488	0.132	0.380	1268	0.948	0.0011	90.21	96.76	68.48	0.185	22.98
0.485	0.315	0.200	1259	0.882	0.0012	91.11	98.29	195.70	0.439	55.89
0.496	0.400	0.104	1256	0.849	0.0012	91.38	98.85	246.57	0.552	69.79
0.584	0.135	0.281	1271	0.925	0.0012	88.96	95.59	74.37	0.200	24.95
0.586	0.223	0.192	1266	0.891	0.0012	89.37	96.33	148.52	0.355	44.37
0.579	0.296	0.125	1262	0.866	0.0012	89.80	97.03	204.60	0.480	59.44
0.677	0.046	0.277	1280	0.936	0.0011	87.32	93.71	4.65	0.091	7.62
0.683	0.120	0.197	1275	0.906	0.0012	87.61	94.28	71.46	0.214	24.72
0.685	0.220	0.095	1269	0.868	0.0012	88.05	95.12	162.92	0.411	49.10
0.801	0.047	0.152	1285	0.905	0.0012	85.72	92.18	0.53	0.099	6.53
0.785	0.120	0.095	1279	0.881	0.0012	86.28	93.04	78.90	0.253	27.07
0.852	0.051	0.098	1287	0.891	0.0012	85.08	91.61	6.15	0.123	8.01
0.048	0.046	0.907	1265	1.075	0.0011	95.50	101.48	−40.39	0.017	−6.18
0.150	0.044	0.806	1267	1.055	0.0011	94.16	100.18	−34.05	0.007	−4.05
0.166	0.092	0.743	1264	1.034	0.0011	94.19	100.35	−4.00	0.046	2.76
0.286	0.182	0.532	1261	0.976	0.0011	93.06	99.58	69.77	0.163	21.30
0.734	0.166	0.101	1274	0.876	0.0012	87.17	94.05	116.60	0.317	36.87
0.693	0.265	0.042	1267	0.849	0.0012	88.18	95.40	193.89	0.473	57.51
0.925	0.035	0.040	1292	0.879	0.0012	84.05	90.54	−20.09	0.085	0.99
0.570	0.073	0.358	1275	0.951	0.0011	88.85	95.25	21.42	0.102	11.49
0.370	0.068	0.562	1270	0.999	0.0011	91.42	97.64	−0.40	0.045	5.11
0.754	0.070	0.176	1281	0.908	0.0012	86.44	92.95	19.53	0.119	11.32
0.107	0.026	0.868	1268	1.070	0.0011	94.64	100.58	−50.73	−0.012	−8.11
0.048	0.187	0.765	1257	1.025	0.0011	96.18	102.55	36.15	0.118	10.47
0.043	0.915	0.043	1249	0.789	0.0012	99.75	107.64	181.04	0.183	39.61
0.171	0.781	0.048	1247	0.800	0.0012	97.44	105.35	240.90	0.407	60.65

For the binary system, benzene + cyclohexane (I), values of three excess functions have been calculated for the entire composition range. For this aromatic alicyclic system, values of E^E and V^E are found to be large as compared to the other systems. Furthermore, values of E^E and V^E are found to follow an increasing trend initially but are found to gradually decrease at higher concentration of benzene. The TS^E values are also found to follow the same trend as that of other excess functions which is clearly indicated from the tables. A certain ordered arrangement seems to be present in liquid benzene which gets disturbed by the addition of a nonaromatic constituent. Thus positive and large values of E^E and TS^{E} are obtained.

In the system benzene + chlorobenzene, a perusal of the table indicates that the values of E^E and V^E are quite less then their corresponding values in the previous

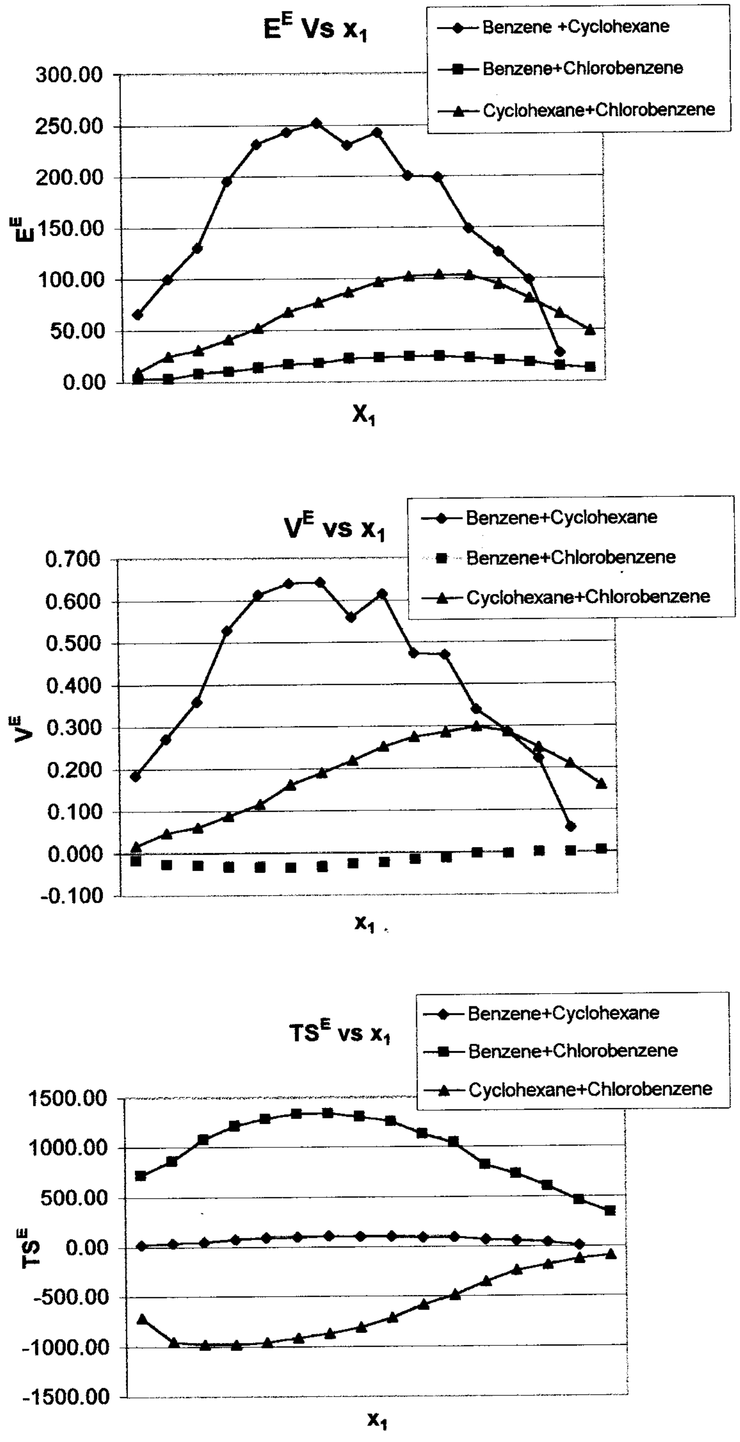

FIGURE 1 Excess entropy (E^E), excess volume (V^E) and excess entropy (TS^E) for the binary systems, benzene + cyclohexane, benzene + chlorobenzene and cyclohexane + chlorobenzene at 298.15 K.

binary system. The values of the excess functions show an initial increase following the trend of the previous system though the TS^E values are found to be peculiarly high. The mixture may be considered as containing a polar liquid, viz., chlorobenzene, however it has been explained [11] that a mixture of benzene with chlorobenzene ($\pi = 1.5\,D$) having moderate dipole moment and reasonable symmetry may be classed as a nonpolar mixture. Furthermore presence of delocalised π electron cloud above and below the benzene ring prevents interaction to a very large extent and thus the system tends towards ideality giving low values of E^E. Also very small negative values of V^E are obtained indicating little interaction between the liquids.

For the system cyclohexane + chlorobenzene, perusal of the values of E^E and V^E indicates that the values of excess functions lie in between those of benzene + cyclohexane and benzene + chlorobenzene. The values of TS^E are found to be skewed towards high mole fractions of cyclohexane (Fig. 1).

In the ternary system, benzene + cyclohexane + chlorobenzene, interactions on basis of excess functions can be explained using the fact that if one of the components is negligible the system as expected starts following the trend set be the resultant binary. In this particular system, benzene and cyclohexane are the key factors in determining the magnitude of excess functions. As shown in Table V even when x_3 is large ≈ 0.90 and x_1 and $x_2 \approx 0.04$, very small values of excess functions are obtained. This fact is also supported by the observation that when x_1 (concentration of benzene) is constant and x_2 and x_3 varying, the excess properties follow the trend set by x_2, i.e., as x_2 increases, E^E and V^E are found to increase despite decreasing concentration of chlorobenzene. On the other hand when x_2 is fixed and x_1, x_3 varying, the excess properties follow the trend set by x_1 values. All the excess properties show an increasing trend with increase in x_1 even when x_3 is decreasing. Minimum values of excess functions are obtained when $x_1 \approx x_3$ and x_2 is small, minimum values are obtained again when cyclohexane concentration i.e. x_2 is large and x_1 and x_3 are found to be comparable.

We thus conclude by saying that the system containing benzene + cyclohexane shows highest degree of interactions as evident from the values of excess functions for the system. Chlorobenzene + benzene on the other hand show small values of E^E and even negative and small excess volumes. The ternary system can be said to be made up of three binary systems and if the concentration of one component is small and fixed the system behaves like the resultant binary. Thus for organic liquid mixtures this predictive method for determining excess functions can be used as a powerful tool from simple data like ultrasonic velocity and density only, by using the Schaaffs equation and some semiempirical methods, one can determine E^E, V^E and TS^E values quite satisfactorily.

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