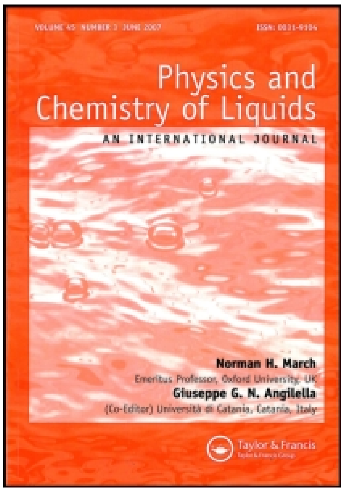

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Pandey, J. D. , Soni, N. K. , Singh, V. K. and Sanguri, V.(2001) 'Surface Tension of Ternary Liquid Mixtures', Physics and Chemistry of Liquids, 39: 6, 763 — 772

To link to this Article: DOI: 10.1080/00319100108031691

URL: http://dx.doi.org/10.1080/00319100108031691

Phys. Chem. Liq., 2001, Vol. 39, pp. 763–772
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SURFACE TENSION OF TERNARY LIQUID MIXTURES

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(Received 29 September 2000)

Surface tension has been measured by the differential capillary rise method for three ternary mixtures containing alkanes (hexane + cyclohexane + benzene, pentane + hexane + benzene and cyclohexane + heptane + toluene at 298.15 ± 0.1°K). The sign and magnitude of the excess surface tension and excess volume depend ultimately upon the chain length of the component of the mixtures. The results of the surface tension were compared with theoretical values obtained from Flory theory, Sanchez method, Brock-Bird relation and volume fraction statistics. There is reasonable agreement between theory and experiment.

Keywords: Surface tension; Flory theory; Volume fraction statistic; Ternary mixtures

INTRODUCTION

Very little work has been done on the experimental measurements of surface tension of multicomponent liquid systems except some papers [1–6] dealing with the ternary liquid mixtures. As an extension of this investigation, we have determined the surface tension of three ternary liquid mixtures, hexane + cyclohexane + benzene 1, pentane + hexane + benzene 2 and cyclohexane + heptane + toulene 3 at 298.15 ± 0.1° K. However, various statistical and empirical approaches *viz.* Flory-Patterson theory [7, 8], Sanchez method [9], Brock-Bird relation [10]

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and volume fraction statistics [11] have also been applied to these ternary mixtures. A comparative study and its correlation with molecular interactions has also been made in the present context. It is hoped that the accumulation of accurate experimental information will ultimately lead to a better understanding of the molecular configuration and molecular interaction of liquid ternary systems.

EXPERIMENTAL METHOD

The component liquids were obtained from B.D.H. Chemicals Ltd. Poole England and they were of AnalaR grade. They were purified once more and distilled according to the methods reported in the literature [12]. Densities were measured at 298.15 ± 0.1° K in a calibrated pyknometer with an accuracy of $0.3\,\mathrm{kg\,m^{-3}}$. Surface tension was measured by the differential capillary rise technique at 298.15 ± 0.1° K with an accuracy of $\pm 7.3 \times 10^{-4}\,\mathrm{Nm^{-1}}$. Results are listed in Table I along with the literature values [13] for comparison. The overall uncertainty in the mole fractions of the mixture is better than $\pm 3 \times 10^{-4}$.

THEORETICAL

Surface tension of ternary liquid mixtures is calculated by Flory-Patterson [7, 8] theory with the help of following expression

$$\sigma = \sigma^{*}\sigma(\mathrm{v}) \tag{1}$$

where σ^{*} and $\sigma(\mathrm{v})$ are characteristic and reduced surface tension.

TABLE I Densities ρ and surface tension σ for the component liquids at 298.15 K

	$\rho(kg\,m^{-3})$		$\sigma(10^{-3}\,Nm^{-1})$	
Component liquids	*obs*	*lit* [13]	*obs*	*lit* [13]
n-pentane	621.6	621.3	15.56	15.50
n-hexane	655.2	655.0	17.99	17.91
Cyclohexane	773.6	773.8	24.01	24.40
Benzene	873.3	873.6	28.99	28.26
n-heptane	679.3	679.5	18.69	19.80
Toluene	862.6	862.5	27.24	27.96

Patterson and Rastogi [14] in their extension of the corresponding state theory defined characteristic surface tension of the liquid mixture as

$$\sigma^* = k^{1/3}P^{*2/3}T^{*1/3} \tag{2}$$

Here **k** is the Boltzmann constant. Starting from the work of Prigogine and Saraga [15] they derived a reduced surface tension which in the case of van der Waals liquid can be written as:

$$\sigma(v) = Mv^{-5/3} - \{(v^{1/3} - 1)/(v^2)\} \ln \{(v^{1/3} - 0.5)/(v^{1/3} - 1.0)\} \tag{3}$$

where M is the fraction of nearest neighbours that a molecule loses on moving from the bulk of the liquid to the surface. Its most suitable value [15] is 0.29, which is used in our calculations.

The characteristic and reduced parameters involved in the above equation can be evaluated by the procedure extended by Pandey and Pant [16] in the case of ternary liquid mixture.

In prediction of surface tension of aforesaid liquid mixtures by Flory-Patterson theory only thermal expansion coefficient and isothermal compressibility of pure components are required. We don't need even the surface tension of pure liquids contributing the mixture.

Sanchez relation [9], which has been applied successfully to binary liquid mixtures, is extended here to deduce the value of surface tension of ternary liquid mixtures. The relation is

$$\sigma(\beta_T/\rho)^{1/2} = A_0^{1/2} \tag{4}$$

here β_T and ρ are isothermal compressibility and mass density of liquid.

If $\beta_{T,i}$ and ρ_i are isothermal compressibility and mass density of the pure components. We can have the following approximations:

$$\beta_i = \Sigma\phi_i\beta_{T,i} \tag{5}$$

$$\rho_i = \Sigma\phi_i\ \rho_i \tag{6}$$

$$A_0 = \Sigma x_i A_i^{1/2} \tag{7}$$

where ϕ_i and x_i are the volume fraction and mole fraction of ith component. A_i is defined as

$$A_i = \sigma^2(\beta_{T,i}/\rho_i) \tag{8}$$

The Brock-Bird relation [10] which predicts the surface tension of a ternary liquid mixture can be written as

$$\{\rho/(P_c^2 T_c)^{1/3}\} = \{-0.951 + (0.432/Z_c)\}(1 - T_r)^{11/9} \tag{9}$$

where P_c, T_c, Z_c and T_r are respectively the critical pressure, critical temperature, critical compressibility factor and reduced temperature of the mixture. These parameters are calculated from the critical constants of pure liquids [8] with aid of following expressions:

$$\begin{aligned} &P_c = \Sigma x_i P_c; \quad T_c = \Sigma x_i T_{c,i}; \quad V_c = \Sigma x_i V_{c,i}; \\ &Z_c = (1/R)(P_c V_c/T_c) \quad \text{and} \quad T_r = (T/T_c) \end{aligned} \tag{10}$$

Goldsach and Sarvas [11] used the mole fraction and volume fraction statistics to obtain the expression for the surface tension of non-electrolyte solutions and applied to various binary organic liquid mixtures. The starting point is to use the following general equation:

$$\Sigma x_{i,s} = \Sigma x_{i,B} \ \exp\{(\sigma - \sigma_i)A_i/RT\} = 1 \tag{11}$$

where $x_{i,s}$ and $x_{i,B}$ are respectively the mole fractions of the ith component in surface and bulk phase. A_i is the molar surface area of the ith component. This equation can be rearranged to obtain the concentration dependence of the surface tension of ternary system as

$$\begin{aligned} &x_{1,B}[\exp(\sigma - \sigma_1)(A_1/RT) + x_{2,B}[\exp(\sigma - \sigma_2)(A_2/RT)] \\ &\quad + x_{3,B}[\exp(\sigma - \sigma_3)(A_3/RT) = 1 \end{aligned} \tag{12}$$

Since the some of the mole fractions in the bulk phase is unity and also $A_3 = A_2 = A_1 = A$, which is an approximations often used in the literature, one obtains

$$\begin{aligned} \sigma = -(RT/A) \ln \, &[x_1 \exp(-\sigma_1 A/RT) + x_2 \exp(-\sigma_2 A/RT) \\ &+ x_3 \exp(-\sigma_3 A/RT)] \end{aligned} \tag{13}$$

where A, the molar surface area, can be obtained from the relation

$$A = \pi\{3/(4\pi)\}^{2/3} N^{1/3} \{(V_1 + V_2 + V_3)/3\}^{2/3} \qquad (14)$$

Here, N being the Avogadro number and V_1, V_2 and V_3 are respective molar volumes of the components 1, 2 and 3.

RESULTS AND DISCUSSION

Mole fractions x_1, x_2, measured surface tension σ, theoretical surface tensions from various models, their percentage deviations, excess volume V_m^E and excess surface tension σ^E for three ternary liquid mixtures are listed in Table III. Excess volume V_m^E and excess surface tension σ^E were calculated from the expression assuming surface tension and volume fraction parameters to be linear in mole fraction of the component.

$$V_m^E = \Sigma(x_i M_i/\rho) - \Sigma x_i V_i \qquad (15)$$

$$\sigma^E = \sigma_{exp} - \Sigma x_i \sigma_i \qquad (16)$$

where symbol 'i' denotes the ith component and ρ is the density of mixture. Table II contains the parameters for the pure component liquids [18]. Numerical evaluation of characteristic parameters for the pure components were carried out according to the procedure adopted by Flory [7, 8].

A careful perusal of Table III appears that volume fraction statistic provides fairly good agreement followed by Flory's statistical theory, Sanchez method and Brock-Bird relation except in the case of hexane + cyclohexane + benzene system.

The corresponding state treatment of the mixtures described is somewhat unorthodox, since application of Eq. (3) to the ternary liquid mixture on the assumption that they are equivalent to single component liquid effectively ignores the differences in concentration occuring at the surfaces of the mixtures. Gibbs enrichment of a mixture surface by the component of the lower surface tension is well known. The normal results show a lowering of mixture's surface tension from a linear function of bulk mole fraction. That is why there is a tendency of our theoretical values to be higher than the

TABLE II Thermal expansion coefficient α, isothermal compressibility β_T, characteristic molar volume V^*, characteristic pressure P^*, characteristic temperature T^*, reduced molar volume V, critical volume V_c critical temperature T_c, critical pressure P_c, and measured surface tension σ_{obs} for the component liquids at 298.15 K

Component liquids	α *kK*	β_T TPa^{-1}	V^* $cm^3\,mole^{-1}$	P^* *GPa*	T^* *K*	$\tilde{V}$ $cm^3\,mole^{-1}$	V_c cm^3mole^{-1}	T_cK	P_c*GPa*	$\sigma_{obs}10^{-3}Nm^{-1}$
n-pentane	1.6226	2123.4	85.1753	0.4232	4144.84	1.3627	304	469.60	0.0336	15.56
n-hexane	1.3897	1709.0	99.4560	0.4240	4432.14	1.3225	370	507.40	0.0297	17.99
Cyclohexane	1.2150	1140.0	84.2919	0.5289	4724.33	1.2902	308	553.40	0.0407	24.01
Benzene	1.2265	967.0	69.2198	0.6316	4702.41	1.2924	259	562.09	0.0489	28.99
n-heptane	1.2589	1424.0	113.6375	0.4441	4642.94	1.2985	432	540.20	0.0273	18.69
Toulene	1.0740	921.5	84.5867	0.5540	5032.94	1.2627	316	591.70	0.0412	27.24
	Ref. [18]	Ref. [18]								

TABLE III Excess volume, excess surface tension, measured surface tension, theoretical surface tension from various methods and their percentage deviations

				Theoretical surface tension $10^{-3} Nm^{-1}$					Percentage deviation (%)			
x1	x2	V_M^E $cm^3 mole^{-1}$ *Eq.* (15)	$\sigma_{exp.}$ $10^{-3} Nm^{-1}$	*Flory theory Eq.* (1)	*Sanchez method Eq.* (4)	*Brock-Bird relation Eq.* (9)	*Volume fraction statistics Eq.* (13)	σ^E $10^{-3} Nm^{-1}$ *Eq.* (16)	*Flory theory*	*Sanchez method*	*Brock-Bird relation*	*Volume fraction statistics*
n-hexane(x1) + cyclohexane(x2) + benzene(x3)												
0.0771	0.4315	−0.0100	25.20	24.00	25.21	24.37	25.95	−0.75	4.76	−0.04	3.29	−2.98
0.1269	0.4149	−0.0101	24.60	23.56	24.56	23.75	25.49	−0.89	4.23	0.16	3.46	−3.62
0.1795	0.3854	−0.0104	24.30	23.14	23.95	23.18	25.06	−0.76	4.77	1.44	4.61	−3.13
0.2279	0.3501	−0.0105	24.00	22.79	23.46	22.70	24.70	−0.70	5.04	2.25	5.42	−2.92
0.2616	0.3341	−0.0001	23.90	22.53	23.10	22.36	24.41	−0.52	5.73	3.35	6.44	−2.13
0.2812	0.3348	0.0000	23.60	22.36	22.88	22.15	24.20	−0.60	5.25	3.05	6.14	−2.54
0.3021	0.3643	−0.0109	23.20	22.13	22.54	21.88	23.83	−0.62	4.61	2.84	5.69	−2.72
0.3062	0.3823	−0.0001	23.00	22.06	22.45	21.81	23.69	−0.69	4.09	2.39	5.17	−3.00
0.3448	0.4566	−0.0109	22.90	21.61	21.80	21.35	22.90	0.00	5.63	4.80	6.77	0.00
0.3231	0.4851	−0.0007	22.10	21.73	21.95	21.50	23.00	−0.70	1.67	0.68	2.71	−4.07
Average percentage deviation									4.58	2.09	4.96	2.7
n-pentane(x1) + n-hexane(x2) + benzene(x3)												
0.0966	0.4171	0.0000	22.60	20.91	21.12	20.60	23.07	−0.47	7.48	6.55	8.85	−2.08
0.1428	0.3739	−0.0104	22.40	20.79	20.93	20.61	22.92	−0.52	7.19	6.56	7.99	−2.32
0.2017	0.3388	−0.0002	21.90	20.49	20.52	20.42	22.52	−0.62	6.44	6.30	6.76	−2.83
0.2590	0.3038	−0.0112	21.60	20.20	20.15	20.25	22.13	−0.53	6.48	6.71	6.25	−2.45
0.2984	0.2877	−0.0105	21.10	19.94	19.85	20.05	21.78	−0.68	5.50	5.92	4.98	−3.22
0.3075	0.2945	−0.0112	20.90	19.81	19.71	19.90	21.59	−0.69	5.22	5.69	4.78	−3.30
0.3420	0.3143	−0.0003	20.70	19.34	19.19	19.43	20.91	−0.21	6.57	7.29	6.14	−1.01
0.3685	0.3523	−0.0112	20.10	18.85	18.66	18.90	20.14	−0.04	6.22	7.16	5.97	−0.20
0.4099	0.3888	−0.0109	19.70	18.26	18.02	18.32	19.19	−0.51	7.31	8.53	7.01	2.59
0.4082	0.4665	−0.0002	18.40	17.80	17.61	17.86	18.36	0.03	3.26	4.29	2.93	0.22

TABLE III (Continued)

				Theoretical surface tension $10^{-3} Nm^{-1}$					Percentage deviation (%)			
*x*1	*x*2	V_M^E $cm^3 mole^{-1}$ *Eq.* (15)	$\sigma_{exp.}$ $10^{-3} Nm^{-1}$	*Flory theory Eq.* (1)	*Sanchez method Eq.* (4)	*Brock-Bird relation Eq.* (9)	*Volume fraction statistics Eq.* (13)	σ^E $10^{-3} Nm^{-1}$ *Eq.* (16)	*Flory theory*	*Sanchez method*	*Brock-Bird relation*	*Volume fraction statistics*
Average percentage deviation									6.17	6.49	6.16	1.74
cyclohexane(x1) + n-heptane(x2) + toluene(x3)												
0.1124	0.3962	0.1043	24.40	23.36	22.34	22.50	23.48	0.91	4.26	8.44	7.79	3.77
0.1760	0.3766	0.0991	24.30	23.30	22.40	22.42	23.45	0.85	4.12	7.82	7.74	3.50
0.2452	0.3379	0.0772	24.20	23.35	22.59	22.53	23.55	0.85	3.51	6.65	6.90	2.69
0.3036	0.3032	0.0797	24.00	23.42	22.78	22.67	23.67	0.33	2.42	5.08	5.54	1.38
0.3479	0.2837	0.0634	23.20	23.41	22.85	22.69	23.69	0.52	−0.91	1.51	2.20	−2.11
0.3760	0.2895	0.0646	24.40	23.29	22.73	22.49	23.55	0.40	4.55	6.84	7.83	3.48
0.3907	0.3050	0.0695	24.50	23.13	22.55	22.24	23.37	0.83	5.59	7.96	9.22	4.61
0.4198	0.3416	0.0791	23.80	22.80	22.18	21.69	21.69	0.84	4.20	6.81	8.87	8.87
0.4468	0.3796	0.0901	23.40	22.47	21.79	21.19	22.55	0.86	3.97	6.88	9.44	3.63
0.4525	0.4393	0.1090	22.80	22.07	21.32	20.52	22.02	0.79	3.20	6.49	10.00	3.42
Average percentage deviation									3.46	6.41	7.53	3.26

experimental values in some cases. However, it would not be proper to say that it is the only reason for the discrepancies. A part of discrepancy may be attributed to the approximation made in the computation of interaction parameters X_{ij}. The results from the statistical theory of Flory can be improved further by considering three body effects also. Spherical nature and possibility of two body interactions have been assumed in defining the equations for segment and site fractions. But there is every possibility of three body interactions also which has been ignored in the present derivation in order to simplify and avoid complexity. Although three body effect contributes very little to the energy of the system, but this probability can not be ignored in spite of spherical nature of the molecule constituting the system under investigation. The probability of three body collisions increases as the area of contact and chain length increases. Therefore, in order to get a comparable results a correction term is needed which include three body effects in the evalution of characteristic and interchange energy parameters in the Flory-Patterson theory.

In the empirical relation of Brock-Bird, uncertainity in the critical constants of the mixture using mole fraction average from the values of their pure components, are considered as a part of discrepancies.

Several mixing rules are proposed to evaluate the critical constants of the mixture depending on the nature of the pure components. The other reason for the discrepancy may be due the fact that the system do not obey the theorem of corresponding states which has been used as basis in the derivation of the relations used under the present investigation.

The excess volume V_m^E of the ternary and quaternary liquid systems [9] can be understood reasonably well on the basis of Flory theory. The magnitude of V_m^E is the results of contributions from physical, chemical and structural factors. The molecular size of the component liquids are almost similar as their characteristic temperature, consequently free volume effect are small and contributions to V_m^E arising from the weak interactions in the system as a whole, leading to positive value of V_m^E as for cyclohexane+n-heptane+toluene. For mixtures comprising comparatively larger chain, free volume contributions will be relatively more significant and negative excess volume might occur for n-hexane+cyclohexane+benzene and n-pentane+n-hexane+benzene.

The excess surface tension σ^E is not always negative. Positive σ^E is also observed at some places in the system n-heptane + n-hexane + benzene which is accounted for the nature and extent of molecular interactions. A look on Table III shows the weak interaction in these ternary systems is supported by Rastogi [20]. Excess thermodynamic properties are the measure of extent of molecular interactions of liquid mixture. Conclusively, statistical approaches are in better agreement than the empirical approaches. The present work satisfies the relative validity of these theories and the experimentation. But the study on the molecular interactions could be made up to some extent due to weak interactions involved in these ternary systems.

Acknowledgement

One of the authors (V S) is thankful to the Council of Scientific and Industrial Research, New Delhi, India for providing financial support.

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