

This article was downloaded by:

On: 28 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

Determination of Kirkwood-Buff integrals of multicomponent liquid mixtures from the speed of sound

Ranjan Dey^a; Richa Verma^b; Tanuja Nautiyal^b; N. K. Soni^b; J. D. Pandey^b

^a Department of Chemistry, BITS-Pilani, Goa Campus, Zuarinagar, Goa, India ^b Department of Chemistry, University of Allahabad, Allahabad, India

To cite this Article Dey, Ranjan , Verma, Richa , Nautiyal, Tanuja , Soni, N. K. and Pandey, J. D.(2009) 'Determination of Kirkwood-Buff integrals of multicomponent liquid mixtures from the speed of sound', *Physics and Chemistry of Liquids*, 47: 3, 287 – 295

To link to this Article: DOI: 10.1080/00319100701785168

URL: <http://dx.doi.org/10.1080/00319100701785168>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Determination of Kirkwood–Buff integrals of multicomponent liquid mixtures from the speed of sound

Ranjan Dey^{a*}, Richa Verma^b, Tanuja Nautiyal^b,
N.K. Soni^b and J.D. Pandey^b

^aDepartment of Chemistry, BITS-Pilani, Goa Campus, Zuarinagar, Goa, India; ^bDepartment of Chemistry, University of Allahabad, Allahabad, India

(Received 14 March 2007; final version received 5 November 2007)

A novel technique has been developed for the determination of Kirkwood–Buff integrals by employing ultrasonic velocity and density only. To the best of our knowledge, there exists no method for the computation of Kirkwood–Buff integrals from ultrasonic velocity and density only for multicomponent liquid mixtures. In this context, K–B integrals have been determined for three ternary mixtures, namely, benzene + cyclohexane + chlorobenzene, benzene + cyclohexane + toluene and toluene + cyclohexane + carbontetrachloride under one atmospheric pressure and 298.15 K by employing a statistical mechanical theory propagated by Arakawa and O. Kiyohara, [Arakawa and O. Kiyohara, Bull. Chem. Soc. Jpn. **43**, 975 (1970)].

Keywords: Kirkwood–Buff integrals; multicomponent; ultrasonic velocity; density

1. Introduction

Measurement of ultrasonic velocity in both liquid and gases can be carried out with a high degree of precision and the data can be correlated to other thermodynamic parameters of liquid mixtures through a set of differential equations. Determination of thermodynamic parameters via this pathway proves to be an attractive one owing to the high precision, accuracy and accessibility of the measurements carried out thereof. A recent increase in the interest of Kirkwood–Buff (K–B) solution theory [1–4] has prompted us to develop a novel technique to determine the K–B integrals using sound speed and density data only. The solution theory of Kirkwood–Buff [5] describes thermodynamic properties of a solution in the entire concentration range, using values of $G_{\alpha\beta}$ defined by

$$G_{\alpha\beta} = \int_0^{\infty} (g_{\alpha\beta}(R) - 1) 4\pi r^2 dr. \quad (1)$$

These are called the K–B integrals, which are related to thermodynamic quantities such as chemical potential, partial molar volumes and isothermal compressibility. Here, $g_{\alpha\beta}(R)$ is the angle averaged pair correlation function and the integral extends over the entire range of intermolecular distances between the pair of molecules of species α and β . It is important to note that as the function, $g_{\alpha\beta}(R)$ reflects the solution structure on the

*Corresponding author. Email: drranjan@hotmail.com

microscopic level, $G_{\alpha\beta}$ values will contain some information about this structure. Also, since the quantities $g_{\alpha\beta}(R)$ cannot be easily measured, the $G_{\alpha\beta}$'s if calculated can provide valuable insight to the structure and interactions of liquid mixtures [6].

Majority of the papers devoted to K–B parameters containing non-electrolyte solutions concern binary mixtures [6–10], work on ternary [11] and multicomponent mixtures is presently scarce. The pioneering work in this field has been recently carried out by Matteoli and Mansoori [8–10]. It appears from literature that sound speed has not been used for the study of the K–B integrals in ternary systems. Direct calculation of these quantities from sound speed and density data for ternary liquid systems form the basis of this article. This has been accomplished by incorporating a statistical mechanical theory advanced by Arakawa and Kiyobara [12] and some curve fitting techniques to make the calculations at atmospheric pressure and at 298.15 K. For this purpose, three ternary mixtures have been selected, namely, benzene + cyclohexane + chlorobenzene, benzene + cyclohexane + toluene and toluene + cyclohexane + carbontetrachloride.

2. Theoretical

The $G_{\alpha\beta}$ values for the ternary mixtures under investigation are related to the thermodynamic quantities by the following equations [1]

$$G_{\alpha\beta} = \frac{1}{\rho_\alpha \rho_\beta} \frac{A^{\alpha\beta}}{\det(A)} - \frac{\delta_{\alpha\beta}}{\rho_\beta},$$

$$A^{\alpha\beta} = \frac{V\mu_{\alpha\beta}}{RT} + \frac{V_\alpha V_\beta}{RT\kappa}. \quad (2)$$

In these expressions, $\det(A)$ is the determinant of the matrix A with the elements $A_{\alpha\alpha}$, $A^{\alpha\beta}$ is the cofactor of the element $A_{\alpha\beta}$, $\delta_{\alpha\beta}$ is the Kronecker δ function; $\rho_\alpha = N_\alpha/V$, where $V = \sum_{\alpha=1}^3 N_\alpha V_\alpha$ is the volume of the system, N_α is the number of moles, V_α is the partial molar volume of the components; and κ is the isothermal compressibility factor. The $\mu_{\alpha\beta}$ values are defined as,

$$\mu_{\alpha\beta} = \left(\frac{\partial \mu_\alpha}{\partial N_\beta} \right)_{T,P,N_{\beta \neq \alpha}}, \quad (3)$$

μ_α is the chemical potential of the α component,

$$\mu_\alpha = \mu_\alpha^\circ + RT \ln \gamma_\alpha X_\alpha. \quad (4)$$

Thus, the evaluation of the K–B parameters entails the experimental values of \overline{V}_α , i.e. the partial molar volumes, number densities and the derivatives of the chemical potential $(\partial \mu_\alpha / \partial N_\beta)_{T,P,N_\gamma}$. In order to calculate these interaction parameters directly using sound speed and density data, the statistical mechanical theory of Arakawa [12–15] was used to calculate the excess functions for ternary systems.

For the partial molar volumes, equation of the following type is generally used to which the V^E data can be fitted. Here the x_1 and x_2 are the mole fractions of the first and second components, respectively.

$$V^E = x_1 x_2 [A_{12} + B_{12}(x_1 - x_2)] + x_2 x_3 [A_{23} + B_{23}(x_2 - x_3)]$$

$$+ x_1 x_3 [A_{13} + B_{13}(x_1 - x_3)] + x_1 x_2 x_3 C_{123}. \quad (5)$$

However, we can assume our mixtures to be regular [15] and can write

$$V^E = x_1x_2A + x_2x_3B + x_1x_3C + x_1x_2x_3D. \quad (6)$$

The coefficients of the above equation are obtained by the least square method. A similar equation was fitted to the excess Gibbs's free energy values.

V^E can be written in terms of molar volume of pure components V_α^* etc. and partial molar volume \bar{V}_α , ($\Delta V_\alpha = \bar{V}_\alpha - V_\alpha^*$) etc., considering x_1 and x_2 to be the two independent variables:

$$V^E = x_1\Delta V_1 + x_2\Delta V_2 + (1 - x_1 - x_2)\Delta V_3. \quad (7)$$

Differentiating w.r.t x_1 and x_2 we get the following equations

$$\begin{aligned} \frac{\partial V^E}{\partial x_1} &= \Delta V_1 - \Delta V_3, \\ \frac{\partial V^E}{\partial x_2} &= \Delta V_2 - \Delta V_3. \end{aligned} \quad (8)$$

Substituting for ΔV_1 and ΔV_2 in Equation (7), ΔV_3 can be obtained leading us to the partial molar volumes. Substituting the values of the partial molar volumes we can obtain the number density from

$$\rho = \sum_{\alpha=1}^3 \rho_\alpha, \quad (9)$$

$$\sum_{\alpha=1}^3 \rho_\alpha \bar{V}_\alpha = 1. \quad (10)$$

The chemical potentials and their various derivatives involved in the calculations have been evaluated using excess Gibbs free energy values [13,14].

$$\mu_\alpha^E = RT \ln \gamma_\alpha \quad \text{and} \quad G^E = RT \sum_{\alpha} n_\alpha \ln \gamma_\alpha. \quad (11)$$

Here we get

$$\Delta\mu_2 = \frac{\partial G^E}{N\partial x_2} + \Delta\mu_3 + RT \ln x_2 - RT \ln x_3 \quad (12)$$

and

$$\Delta\mu_1 = \frac{\partial G^E}{N\partial x_1} + \Delta\mu_3 + RT \ln x_1 - RT \ln x_3. \quad (13)$$

The $\Delta\mu_3$ can be evaluated using

$$\frac{G^E}{N} = \frac{x_1}{N} \frac{\partial G^E}{\partial x_1} + \frac{x_2}{N} \frac{\partial G^E}{\partial x_2} + \Delta\mu_3 - RT \ln x_3, \quad (14)$$

also

$$\frac{\partial \mu_1}{\partial x_1} = \frac{\partial \Delta\mu_1}{\partial x_1}, \quad \frac{\partial \mu_2}{\partial x_2} = \frac{\partial \Delta\mu_2}{\partial x_2} \quad \text{and} \quad \frac{\partial \mu_3}{\partial x_3} = \frac{\partial \Delta\mu_3}{\partial x_3}. \quad (15)$$

All the quantities calculated from the above procedure have been substituted in Equation (2) and after some intricate calculations; we obtained the K–B parameters.

3. Results and discussion

Ultrasonic speed and density data for the ternary systems benzene + cyclohexane + chlorobenzene (I), benzene + cyclohexane + toluene(II) and toluene + cyclohexane + carbontetrachloride(III) have been taken from various [11,12] sources. The excess enthalpies and entropies have been calculated through the Arakawa's statistical mechanical theory for the same [11,12] and the free energy values ($E^E - TS^E$) are used here to obtain the chemical potential derivatives. The data of pure components are given in Table 1. The calculated values of the K–B parameters are represented graphically and recorded in Tables 2–4.

Table 1. Molecular parameters of pure liquids at 298.15 K.

Components	Molecular weight	u (ms ⁻¹)	ρ (g cc ⁻¹)
Toluene	92.14	1304.3	0.8626
Cyclohexane	84.16	1252.0	0.7736
Carbontetrachloride	153.82	926.0	1.5851
Benzene	78.14	1295.3	0.8736
Chlorobenzene	113.64	1268.0	1.0080

Table 2. Kirkwood–Buff parameters for ternary liquid mixture: benzene (x_1) + cyclohexane (x_2) + chlorobenzene at 298.15 K.

x_1	x_2	u (ms ⁻¹)	ρ (g cc ⁻¹)	G_{11}	G_{22}	G_{33}
0.071	0.424	1247	0.94	-742.77	-204.01	-176.36
0.072	0.231	1255	1.01	-1869.06	-606.82	-167.93
0.072	0.525	1244	0.91	-5347.06	-317.75	-447.69
0.077	0.619	1243	0.87	-1890.29	-180.75	-383.34
0.083	0.804	1246	0.81	-2819.84	-148.21	-1480.98
0.165	0.327	1252	0.95	-556.40	-283.69	-187.70
0.167	0.718	1246	0.82	-931.06	-160.11	-1337.83
0.288	0.228	1258	0.96	-500.73	-777.98	-301.55
0.293	0.599	1248	0.83	-34.46	-116.94	584.64
0.390	0.130	1266	0.97	-232.93	-556.47	-183.17
0.392	0.313	1256	0.90	-236.41	-294.87	-305.41
0.399	0.402	1253	0.87	-181.50	-199.94	-268.78
0.482	0.048	1274	0.98	-195.20	-1587.15	-197.56
0.488	0.132	1268	0.95	-160.53	-286.66	-174.31
0.496	0.400	1256	0.85	-108.98	-170.06	456.38
0.584	0.135	1271	0.92	-180.79	-915.05	-414.97
0.586	0.223	1266	0.89	-143.56	-351.49	-338.14
0.677	0.046	1280	0.94	-135.84	-1738.04	-323.62
0.683	0.120	1275	0.91	-145.51	-902.03	-552.93
0.685	0.220	1269	0.87	-132.64	-407.85	-779.25
0.852	0.051	1287	0.89	-103.00	-1393.55	-694.53

Table 3. Kirkwood–Buff parameters for ternary liquid mixture: benzene (x_1) + cyclohexane (x_2) + toluene at 298.15 K.

x_1	x_2	u (ms ⁻¹)	ρ (g cc ⁻¹)	G_{11}	G_{22}	G_{33}
0.133	0.212	1291	0.84	-942.04	-724.87	-174.44
0.164	0.230	1269	0.84	-581.40	-368.05	-165.10
0.185	0.246	1268	0.84	-493.44	-326.96	-173.52
0.230	0.283	1268	0.84	-365.90	-266.84	-198.50
0.297	0.334	2165	0.83	-342.51	-304.93	-277.25
0.339	0.374	1259	0.83	-330.94	-298.44	-360.60
0.361	0.391	1265	0.83	-237.20	-222.74	-398.67
0.382	0.409	1265	0.83	760.44	562.05	-304.70
0.405	0.418	1272	0.82	-176.57	-182.86	-555.66
0.444	0.436	1278	0.82	-102.14	-129.07	-828.46
0.465	0.422	1254	0.83	-30.53	-55.07	-690.73
0.507	0.362	1260	0.83	-165.88	-217.55	-593.94
0.527	0.343	1265	0.83	-198.80	-317.20	-864.40
0.578	0.297	1273	0.84	-180.78	-389.24	-1070.26
0.604	0.268	1286	0.84	-157.21	-337.04	-638.99
0.624	0.246	1295	0.84	-153.29	-372.25	-649.28
0.643	0.230	1284	0.84	-147.88	-385.37	-597.51
0.662	0.212	1280	0.85	-137.82	-206.42	382.77
0.680	0.194	1254	0.85	-141.83	-620.06	-1311.66
0.697	0.176	1258	0.85	-136.73	-481.13	-515.60
0.704	0.165	1268	0.85	-133.54	-944.05	-1957.90

Table 4. Kirkwood–Buff parameters for ternary liquid mixture: toluene (x_1) + cyclohexane (x_2) + carbontetrachloride at 298.15 K.

x_1	x_2	u (ms ⁻¹)	ρ (g cc ⁻¹)	G_{11}	G_{22}	G_{33}
0.113	0.204	984	1.32	-839.06	-455.90	-150.37
0.127	0.224	998	1.28	-710.41	-406.62	-164.58
0.154	0.300	1021	1.21	-729.09	-350.55	-179.22
0.173	0.263	1094	1.22	-618.82	-397.96	-176.17
0.191	0.282	1055	1.19	-723.84	-417.32	-154.07
0.213	0.303	1064	1.16	-511.07	-346.55	-205.78
0.232	0.326	1077	1.11	-353.52	-301.93	-272.43
0.252	0.344	1139	1.09	-381.40	-297.11	-273.72
0.274	0.362	1146	1.06	-363.39	-287.46	-301.43
0.297	0.386	1157	1.02	-297.24	-267.15	-387.28
0.313	0.408	1168	1.00	-451.43	-274.22	-249.64
0.336	0.428	1148	0.97	-262.11	-243.83	-551.83
0.357	0.441	1215	0.94	-4.16	-217.49	-1334.25
0.376	0.450	1235	0.92	-318.29	-241.94	-490.47
0.396	0.461	1242	0.90	-304.54	-236.23	-550.89
0.417	0.469	2151	0.88	-267.65	-231.54	-862.94
0.418	0.454	1247	0.90	-307.19	-239.23	-404.09
0.493	0.349	1234	0.92	-207.36	-310.75	-774.40
0.539	0.296	1180	0.93	-206.71	-354.19	-564.06
0.623	0.230	1176	0.93	-174.86	-441.50	-699.68
0.655	0.194	1169	0.93	-161.65	-589.76	-654.10

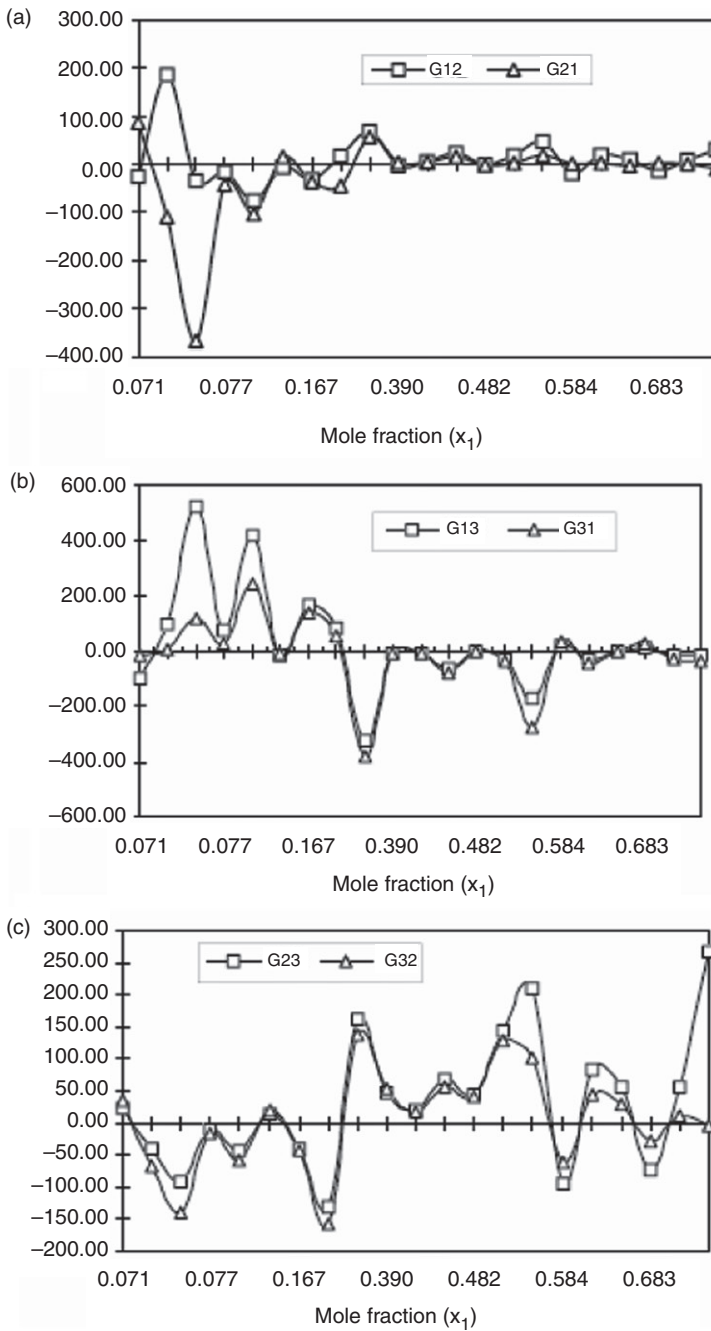


Figure 1. Kirkwood-Buff parameters for ternary liquid mixture benzene (x_1) + cyclohexane (x_2) at 298.15 K.

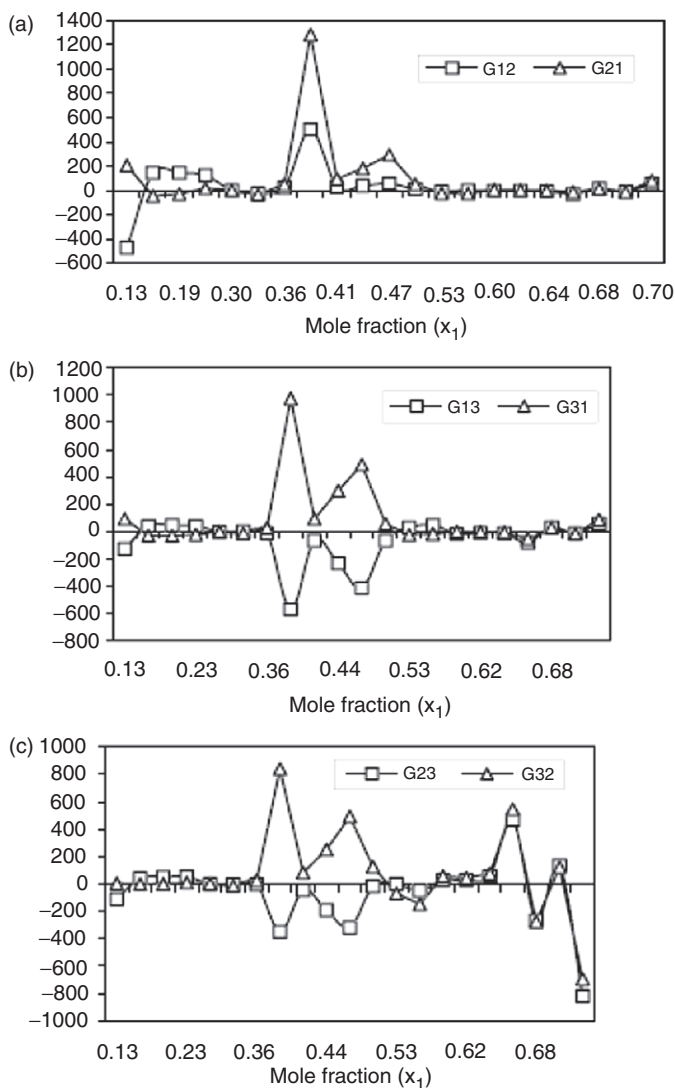


Figure 2. Kirkwood–Buff parameters for ternary liquid mixture benzene (x_1) + cyclohexane (x_2) + toluene (x_3) at 298.15 K.

As evident in Tables 2–4, the self-interaction depicted by the $G_{\alpha\alpha}$'s are comparatively much more negative than the $G_{\alpha\beta}$'s in all the systems. The close perusal of the Table 2 indicates that the benzene–benzene interaction (G_{11}) shown by the system I is found to have the largest numerical value, around the mole fraction 0.07. Peaks in the G_{12} and G_{13} curves are found to be near this mole fraction indicating that the benzene–benzene interaction plays an important role in the $G_{\alpha\beta}$ calculations. In the system (II) benzene + cyclohexane + toluene, G_{11} and G_{22} both show a maxima at $x_1 = 0.38$, subsequently a distinct peak is observed in all the $G_{\alpha\beta}$ graphs near about this mole fraction. The $G_{\alpha\beta}$ values are the maximum for this system depicting the interaction between unlike particles. The peaks in the $G_{\alpha\beta}$ curves for the system

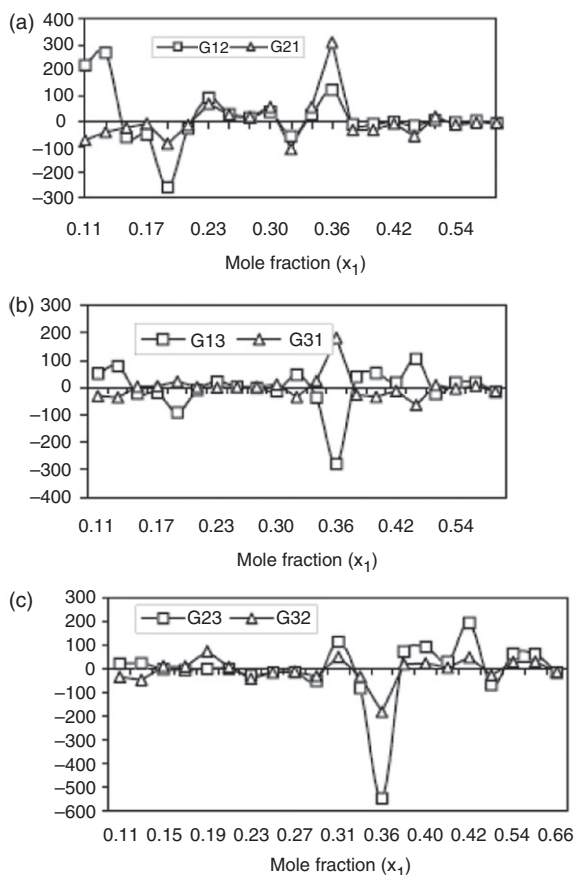


Figure 3. Kirkwood–Buff parameters for ternary liquid mixture; benzene (x_1) + cyclohexane (x_2) + carbontetrachloride at 298.15 K.

toluene + cyclohexane + carbon tetrachloride (III) are sharply defined around the concentration $x_1 = 0.36$.

Ideally in the above calculations the $G_{\alpha\beta} = G_{\beta\alpha}$, i.e. the curves of the parameters should superimpose. However, although the parameters followed the same general trend (Figures 1–3) there are certain differences in the curves. The error seems to lie in the calculations of the chemical potential derivatives and also in the matrix formulation. It is observed however, that as a function of concentration the K–B parameters show extrema in the studied concentration range and the turning point in the graphs can be used to describe the correlation between the pairs of molecules found in the ternary mixtures. (A ternary mixture may be considered as a combination of three binary systems). The significance of this work mainly lies in the direct prediction of these parameters using the ultrasonic speed and density data only.

Acknowledgements

Author J.D. Pandey is thankful to UGC, New Delhi, for the award of Emeritus Fellowship and author N.K. Soni is thankful to CSIR, New Delhi, for financial support.

References

- [1] I.L. Shulgin and E. Ruckenstein, *J. Phys. Chem. B* **110** (5), 12707 (2006).
- [2] P.E. Smith, *Biophys. J.* **91**, 849 (2006).
- [3] A. Parera, F. Sokolic, L. Almasy, P. Westh, and Y. Koga, *J. Chem. Phys.* **123**, 024503 (2005).
- [4] J.N. Canongia Lopes and G. Jansco, *J. Mol. Liq.* **112**, 147 (2004).
- [5] J.G. Kirkwood and F.P. Buff, *J. Chem. Phys.* **19**, 774 (1951).
- [6] A. Ben-Naim, *J. Chem. Phys.* **67** (11), 4884 (1977).
- [7] J.D. Pandey and R. Verma, *Chem. Phys.* **270**, 429 (2001).
- [8] E. Matteoli, E.Z. Hamad, and G.A. Mansoori, in *Equations of State for Fluids and Fluid Mixtures*, edited by J.V. Sengers, R.F. Kayser, C.J. Peters, and H.J. White (Elsevier Science, Amsterdam, 2000), p. 359.
- [9] E.Z. Hamad, U.A. El-Nafaty, and G.A. Mansoori, *Fluid Phase Equilibria* **79**, 21 (1992).
- [10] E. Matteoli and G.A. Mansoori, *J. Chem. Phys.* **103** (11), 4672 (1995).
- [11] J. Zielkiewicz, *J. Phys. Chem.* **99**, 3357 (1995).
- [12] K. Arakawa and O. Kiyohara, *Bull. Chem. Soc. Jpn.* **43**, 975 (1970).
- [13] J.S. Rowlinson and F.L. Swinton, *Liquids and Liquid Mixtures*, 3rd ed. (Butterworth Scientific, London, 1982).
- [14] J.D. Pandey, R. Verma, and R. Dey, *Acoustics Lett.* **24**, 5 (2000).
- [15] J.D. Pandey, R. Dey, and R. Verma, *Phys. Chem. Liq.* **14** (2), 145 (2003).