

Application of the Kirkwood–Buff theory of solutions to acetonitrile + amide binary mixtures by using inversion procedure and regular solution theory

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Abstract. The Kirkwood–Buff (K–B) integrals play an important role in characterizing the intermolecular interactions in liquid mixtures. These are represented by the K–B parameters, G_{AA} , G_{BB} , and G_{AB} , which reflect correlation between like–like and like–unlike species in the mixture. The K–B integrals of binary mixtures of acetonitrile (ACN) with formamide (FA), N,N-dimethylformamide (DMF), N-methylacetamide (NMA) and N,N-dimethylacetamide (DMA) at 298.15 K and at atmospheric pressure have been computed from the experimental data of ultrasonic speed and density. We have used the similar inverse procedure (as proposed by Ben–Naim) to compute the K–B Parameters of the mixtures, in which thermodynamic information on mixtures such as partial molar volumes, isothermal compressibility, and experimental data of partial vapour pressures are used. A new route has been incorporated by using regular solution theory in the computation of excess free energy for obtaining the partial vapour pressures of binary liquid mixtures. The low values of excess entropy ($S^E \approx 0$) obtained for these mixtures indicate the applicability of regular solution theory to these mixtures. The results obtained regarding intermolecular interaction in all the four mixtures under study from this new procedure are in good agreement with those obtained from the trends exhibited by the excess functions of these mixtures.

Keywords. Kirkwood–Buff integrals; binary liquid mixtures; acetonitrile; amide; intermolecular interactions.

1. Introduction

Theoretical prediction of the physicochemical properties of multi-component liquid systems involves an interdisciplinary interest and proved to be an excellent qualitative and quantitative tool for elucidating the molecular structure and nature and extent of interactions in liquid systems. A large amount of experimental data exists, in the literature, on the physicochemical, thermodynamic, transport, acoustic and spectroscopic properties of multi-component liquid systems.^{1–10} But in contrast to this vast experimental work, there exist very few theoretical works on the elucidation of molecular structure and estimation of thermodynamic properties of liquid mixtures. Recently, researchers in this field have been focusing their interest more sharply on the molecular structure along with some representative macroscopic properties that serves to characterize it.^{11,12}

Kirkwood and Buff¹³ theory of solutions relates the radial distribution functions of various molecular

species in a mixture to the derivatives of the thermodynamic properties of the species. This is a general statistical mechanical theory of solutions which is applicable to all types of intermolecular interactions and is valid both classically and quantum mechanically. It is one of the most accepted theories of solutions that directly correlate the thermodynamic quantities with the solution structure without any assumptions. K–B theory, being a powerful tool for liquid state theory, has not received much attention in thermodynamic literature, as it deserves. Only few examples of practical applications^{14–28} to binary mixtures can be found in which this theory has been to be used only for aqueous-alcohol^{14,18–22} binary mixtures and aqueous solutions containing electrolytes.^{23,24} To the best of our knowledge, very few studies have been made in the literature on non-aqueous binary mixtures.^{25–28} The main objective of the present study is to apply the K–B theory to the systems of varied nature in order to extract new information on the interactions between the species existing in these systems on molecular level.

In this paper, the K–B theory has been extended to binary mixtures of acetonitrile (ACN) with formamide (FA), N,N-dimethylformamide (DMF), N-methylacetamide (NMA) and N,N-dimethylacetamide (DMA) at 298.15 K and at atmospheric pressure. Some new routes for predicting various parameters/terms involved in K–B theory have also been incorporated and effectively used. The experimental data required for this purpose are taken from our previous studies.^{29,30}

2. Theory

The solution theory proposed by Kirkwood and Buff¹³ involves the theory of the grand ensembles on the one hand to relate compositional fluctuations to the derivatives of the chemical potentials of the components and on the other hand to relate them to the integrals of the radial distribution functions of the several type of molecular pairs present in the solution. The K–B theory describes thermodynamic properties of a solution in the whole concentration range using the values of $G_{\alpha\beta}$, expressed as K–B integrals, given by

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

where $g_{\alpha\beta}(r)$ 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 . The interpretation of these parameters is best obtained by considering the product of number density, ρ^* and $G_{\alpha\beta}$, i.e., $\rho_\alpha G_{\alpha\beta}$ or $\rho_\alpha [g_{\alpha\beta}(r) - 1] 4\pi r^2 dr$, where ρ_α is the number density of the α species.¹⁴ The quantity $G_{\alpha\beta}$ conveys information of the average affinity of the α molecules towards β molecules and vice-versa. In the present study we have incorporated a new method, in the inversion procedure proposed by Ben–Naim,¹⁴ for the computation of partial vapour pressures of the mixtures for which these vapour pressure data are not available. The composition dependence of $G_{\alpha\beta}$ values provides valuable insight into the molecular structure and nature of interactions in the multi-component liquid mixture.

2.1 Inversion procedure to compute $G_{\alpha\beta}$'s

The K–B equations^{13,14} for the binary mixture of species A and B can be written as

$$\eta = \rho_A + \rho_B + \rho_A \rho_B (G_{AA} + G_{BB} - 2G_{AB}), \quad (2)$$

$$\xi = 1 + \rho_A G_{AA} + \rho_B G_{BB} + \rho_A \rho_B (G_{AA} G_{BB} - G_{AB}^2), \quad (3)$$

where η and ξ are constants, ρ_A and ρ_B are the number densities of A and B , respectively. The isothermal compressibility, k_T , the partial molar volumes, $\bar{V}_{m,A}$ and $\bar{V}_{m,B}$ of the two components and derivatives of the chemical potentials are given by

$$k_T = \xi/kT\eta, \quad (4)$$

$$\bar{V}_{m,A} = [1 + \rho_B (G_{BB} - G_{AB})]/\eta, \quad (5)$$

$$\bar{V}_{m,B} = [1 + \rho_A (G_{AA} - G_{AB})]/\eta, \quad (6)$$

$$\mu_{AA} = \rho_B kT/\rho_A \eta V, \quad (7)$$

$$\mu_{BB} = \rho_A kT/\rho_B \eta V, \quad (8)$$

$$\mu_{AB} = \mu_{BA} = -kT/\eta V, \quad (9)$$

where k is the Boltzmann constant, T is the absolute temperature and $\mu_{\alpha\beta}$ is given by

$$\mu_{\alpha\beta} = \left(\frac{\partial \mu_\alpha}{\partial N_\beta} \right)_{T, p, N_\alpha}. \quad (10)$$

We have three thermodynamic relations between the number densities, chemical potentials and partial molar volumes of the two components of the mixture, given as

$$\rho_A \mu_{AA} + \rho_B \mu_{AB} = 0, \quad (11)$$

$$\rho_A \mu_{AB} + \rho_B \mu_{BB} = 0, \quad (12)$$

$$\rho_A \bar{V}_{m,A} + \rho_B \bar{V}_{m,B} = 1. \quad (13)$$

Therefore, we have three independent equations in the three independent unknown $G_{\alpha\beta}$'s. The derivatives of the chemical potentials have been obtained using the vapour pressure data, assuming that the vapour above the mixture at room temperature may be treated as an ideal gas. Thus, for component A , we can write

$$\mu_A = \mu_A^\circ + kT \ln P_A, \quad (14)$$

where P_A is the partial pressure of component A over the given mixture of A and B . If x_A is the mole fraction of A in the mixture, then we get the relation

$$x_A \left(\frac{\partial p_A}{\partial x_A} \right) = \frac{\rho^*}{\eta} \quad (15)$$

The number density, ρ^* , of the mixture is calculated from the partial molar volumes, $\bar{V}_{m,A}$ and $\bar{V}_{m,B}$ of the components A and B , respectively, in the mixtures.

$$\rho^* = \rho_A + \rho_B = (x_A \bar{V}_{m,A} + x_B \bar{V}_{m,B})^{-1} \quad (16)$$

The values of $\bar{V}_{m,A}$ and $\bar{V}_{m,B}$ in the mixtures are calculated from the experimental density data by using the procedure described elsewhere.³⁰

From (15) we can obtain η from the data on partial vapour pressures of either A or B in the entire composition range. The partial vapour pressures are calculated from the activity coefficients, which are related to the excess Gibbs free energy of the mixture. The excess free energy of mixtures is given as

$$G^E = H^E - TS^E \quad (17)$$

The excess enthalpies, H^E and excess entropies, $-S^E$ are calculated from the internal pressures, π_i and free volumes, V_f of the mixtures by using the modified relations proposed by Hildebrand *et al.*^{31,32}

$$H^E = \pi_i V_m - [x_A \pi_{i,A} V_{m,A} + x_B \pi_{i,B} V_{m,B}], \quad (18)$$

$$-S^E = R[x_A \ln V_{f,A} + x_B \ln V_{f,B} - \ln V_{f,m}], \quad (19)$$

where π_i of the mixtures are calculated using the thermodynamic equation of state

$$\pi_i = \left(\frac{\partial E}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P = T \left(\frac{\alpha_p}{k_T} \right) - P, \quad (20)$$

where α_p is the isobaric expansivity of the mixture evaluated from temperature dependence of density data. For most of the liquids, the thermal pressure coefficient multiplied by absolute temperature, i.e. $T(\alpha_p/k_T)$ is very high so that the external pressure P becomes negligible in comparison,^{33,34} therefore it may be neglected in the (20) in the present calculations. The V_f of the mixtures are calculated from the relation^{31,32}

$$V_f = \frac{RT}{(P + \pi_i)}, \quad (21)$$

since P is very small as compared to π_i , it has been neglected in the (21) in the present calculations. The systems are assumed to be ‘regular’ mixtures, for which G^E are given by

$$G^E = x_A x_B Nw, \quad (22)$$

where w is a constant computed from (22), which may depend on temperature but is independent of composition. The activity coefficients in a regular mixture are given by

$$\ln \gamma_i = (1 - x_i)^2 w/kT. \quad (23)$$

The partial vapour pressures of the components in the mixtures are calculated using the activity coefficients. Using the mole fraction dependence of partial vapour pressure of either A or B , η over the entire composition range can be easily obtained from (15). The values of ξ are evaluated from (4), in which the isothermal compressibility, κ_T , is calculated using the well-known thermodynamic relation

$$\kappa_T = k_s + \frac{TV\alpha_T^2}{C_p}, \quad (24)$$

where k_s is isentropic compressibility and C_p is the heat capacity. The C_p values for the mixtures have been calculated by using the relation

$$C_p = x_A C_{p,A} + x_B C_{p,B}. \quad (25)$$

Using the values of η , ξ , $\bar{V}_{m,A}$ and $\bar{V}_{m,B}$, the G_{AB} is calculated using the relation

$$\bar{V}_{m,A} \bar{V}_{m,B} = (\xi - \eta G_{AB})/\eta^2. \quad (26)$$

Once G_{AB} is obtained, (5) and (6) are used to calculate G_{AA} and G_{BB} .

Another quantity proposed by Ben-Naim,¹⁴ Δ_{AB} , which is a measure of the ‘degree of similarity’ between the two components of the mixture, has also been calculated by using the following equation

$$\Delta_{AB} = G_{AA} + G_{BB} - 2G_{AB}. \quad (27)$$

The condition $\Delta_{AB} = 0$ signifies symmetrical ideal solutions. The magnitude of Δ_{AB} can be used to indicate the extent of deviation from ideal behaviour.

The above procedure has been used to calculate the K–B parameters for ACN + FA, + DMF, + NMA and + DMA binary mixtures directly from ultrasonic speed and density data at 298.15 K.

Table 1. Values of ρ , u , p , k_s , k_T , α_p , and C_p for pure liquids at 298.15 K used in the calculation of K–B parameters.

Liquid	ρ (kg m ⁻³)	u (m s ⁻¹)	p (N m ⁻²)	k_s (10 ⁻¹⁰ m ² N ⁻¹)	k_T (10 ⁻¹⁰ m ² N ⁻¹)	α_p (10 ⁻³ K ⁻¹)	C_p (J mol ⁻¹)
ACN	776.6	1282.9	11840.36	7.822	11.116	1.372	90.03
FA	1129.0	1601.0	66.66	3.456	4.118	0.775	107.8
DMF	944.6	1468.3	493.29	5.048	6.575	0.999	150.8
NMA	950.1	1398.8	127.99	5.356	6.379	0.874	170.5
DMA	936.5	1462.6	173.32	4.992	6.426	0.894	154.5

Table 2. Values of ρ , u , ρ^* , H^E , TS^E , $\ln(P_A)$, η , G_{AB} , G_{AA} , G_{BB} and Δ_{AB} for ACN + amide mixtures at 298.15 K.

x_A	ρ (kg m ⁻³)	u (m s ⁻¹)	ρ^* (m ⁻³)	H^E (J mol ⁻³)	TS^E (J mol ⁻³)	$\ln(p_A)$	η (m ⁻³)	G_{AB}	G_{AA}	G_{BB}	Δ_{AB}
								(10 ⁻⁴ m ³ mol ⁻¹)			
ACN + FA											
0.0764	1099.7	1591.3	24582	900.20	-105.29	6.551	52738	-1.060	-0.574	7.768	9.314
0.1610	1068.1	1581.3	24062	1720.30	-200.92	7.320	27450	-0.555	-0.509	0.463	1.064
0.2485	1035.7	1564.9	23512	2246.86	-263.75	7.778	19847	-0.404	-0.524	-0.372	-0.089
0.3444	999.7	1539.0	22894	2469.78	-291.82	8.131	16516	-0.337	-0.570	-0.520	-0.415
0.4120	974.3	1516.8	22454	2453.01	-291.60	8.330	15564	-0.318	-0.613	-0.522	-0.499
0.5336	930.0	1475.1	21671	2254.70	-272.26	8.622	15863	-0.324	-0.702	-0.469	-0.524
0.6388	893.0	1434.5	21014	1884.50	-231.91	8.831	18842	-0.383	-0.741	-0.390	-0.364
0.7554	853.4	1387.9	20309	1369.88	-172.01	9.031	31901	-0.646	-0.195	-0.200	0.895
0.8754	814.5	1336.9	19610	723.92	-92.49	9.212	48896	-2.997	16.123	-1.003	23.120
ACN + DMF											
0.1303	930.1	1431.8	18954	268.29	-49.45	7.100	31243	-1.261	-0.405	1.359	3.477
0.2586	914.5	1413.6	18984	450.95	-89.19	7.821	18402	-0.743	-0.445	-0.825	0.217
0.3851	897.4	1393.2	19013	541.56	-116.48	8.255	14822	-0.599	-0.476	-0.914	-0.191
0.5125	878.4	1371.0	19043	574.43	-133.06	8.576	13924	-0.564	-0.484	-0.847	-0.204
0.5925	865.2	1355.8	19062	554.04	-135.13	8.743	14282	-0.578	-0.451	-0.805	-0.099
0.6899	847.8	1336.5	19085	503.37	-129.59	8.922	15842	-0.641	-0.286	-0.770	0.226
0.7736	831.1	1318.8	19105	424.83	-113.87	9.060	18837	-0.761	0.214	-0.766	0.970
0.8522	813.9	1301.2	19124	321.29	-88.62	9.179	24872	-1.001	1.981	-0.807	3.176
0.9359	793.8	1281.4	19144	178.12	-48.39	9.295	43782	-1.753	15.740	-1.016	18.230
ACN + NMA											
0.1232	940.3	1396.5	18981	738.54	-75.40	7.042	31751	-1.257	-0.402	1.616	3.728
0.2665	922.5	1389.6	19049	1330.87	-144.17	7.853	17646	-0.700	-0.452	-0.878	0.070
0.3702	908.3	1384.2	19098	1664.02	-187.06	8.211	14860	-0.590	-0.479	-0.928	-0.227
0.4925	889.6	1373.2	19156	1811.38	-215.56	8.531	13946	-0.555	-0.491	-0.856	-0.237
0.5800	874.6	1365.1	19198	1844.61	-227.52	8.719	14389	-0.573	-0.460	-0.804	-0.117
0.6766	856.3	1353.2	19245	1724.94	-222.79	8.899	16152	-0.643	-0.303	-0.763	0.219
0.7613	838.4	1340.8	19286	1503.84	-202.31	9.041	19667	-0.781	0.194	-0.757	1.000
0.8305	822.4	1327.1	19319	1186.52	-166.48	9.147	25792	-1.021	1.596	-0.792	2.846
0.9203	799.5	1306.4	19363	647.65	-96.16	9.274	52524	-2.065	14.828	-1.059	17.898
ACN + DMA											
0.1674	921.8	1443.5	18990	497.24	-59.93	7.361	27450	-1.349	-0.371	0.102	2.429
0.3133	906.7	1426.7	19048	889.49	-109.88	8.028	17482	-0.859	-0.385	-0.990	0.344
0.4223	893.8	1413.7	19092	1134.01	-143.88	8.357	15128	-0.744	-0.380	-0.998	0.110
0.5387	877.9	1396.1	19139	1234.82	-166.07	8.633	14407	-0.708	-0.331	-0.944	0.141
0.6379	862.2	1377.9	19179	1191.55	-170.88	8.830	14877	-0.731	-0.195	-0.909	0.359
0.7236	846.7	1361.2	19214	1101.98	-166.31	8.979	16227	-0.798	0.126	-0.902	0.820
0.8071	829.0	1342.2	19248	914.15	-145.17	9.112	18905	-0.929	1.021	-0.930	1.950
0.8776	812.0	1323.8	19277	673.47	-111.86	9.215	23234	-1.142	3.518	-1.006	4.796
0.9424	794.3	1303.7	19303	358.64	-62.43	9.304	31295	-1.538	14.631	-1.178	16.530

3. Results and discussion

The values of K–B parameters for the above-mentioned binary systems have been calculated as a function of mole fraction, x_A of component A (ACN) at 298.15 K. The values of various parameters of pure liquids used in the calculations are listed in

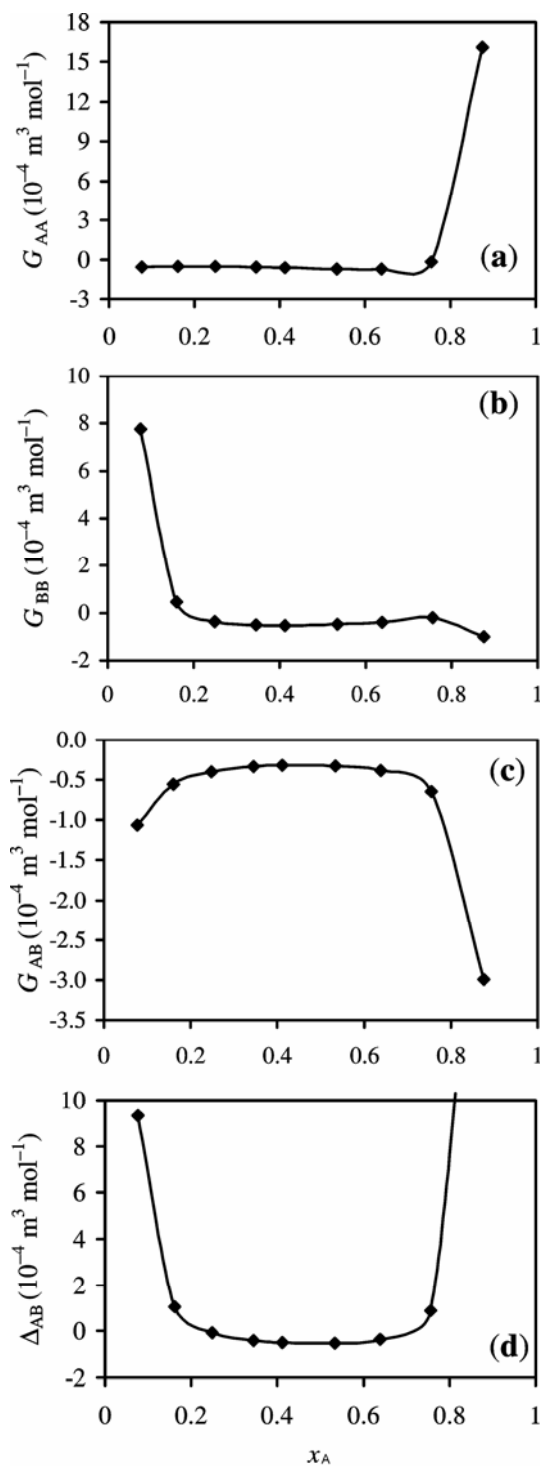


Figure 1. Plots of G_{AA} , G_{BB} , G_{AB} and Δ_{AB} against mole fraction, x_A of ACN for ACN + FA mixtures at 298.15 K.

table 1. The values of K–B parameters, viz. G_{AA} , G_{BB} , G_{AB} and Δ_{AB} along with some other parameters for the binary systems investigated as function of mole fraction, x_A of ACN for each system, are listed in table 2. The variations of G_{AA} , G_{BB} , G_{AB} and Δ_{AB}

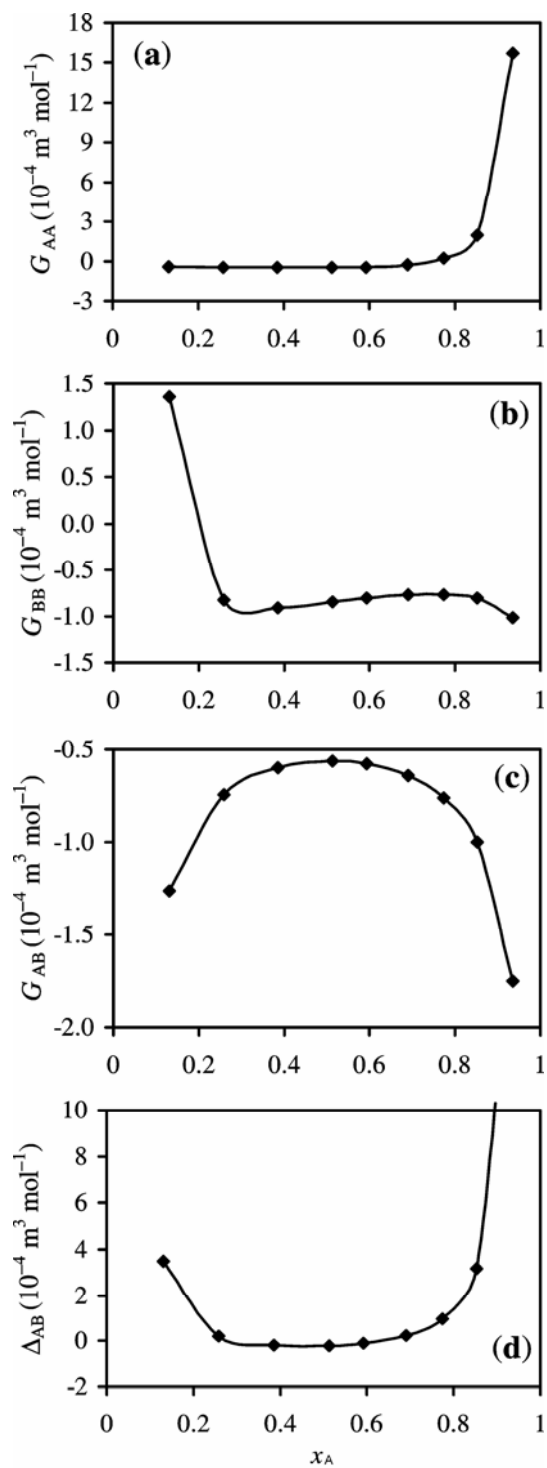


Figure 2. Plots of G_{AA} , G_{BB} , G_{AB} and Δ_{AB} against mole fraction, x_A of ACN for ACN + DMF mixtures at 298.15 K.

against mole fraction, x_A of ACN for each mixture are shown graphically in figures 1–4. The low values excess entropy ($S^E \approx 0$) obtained for these systems (table 2) clearly indicate that these mixtures can be considered as regular solutions.^{31,32}

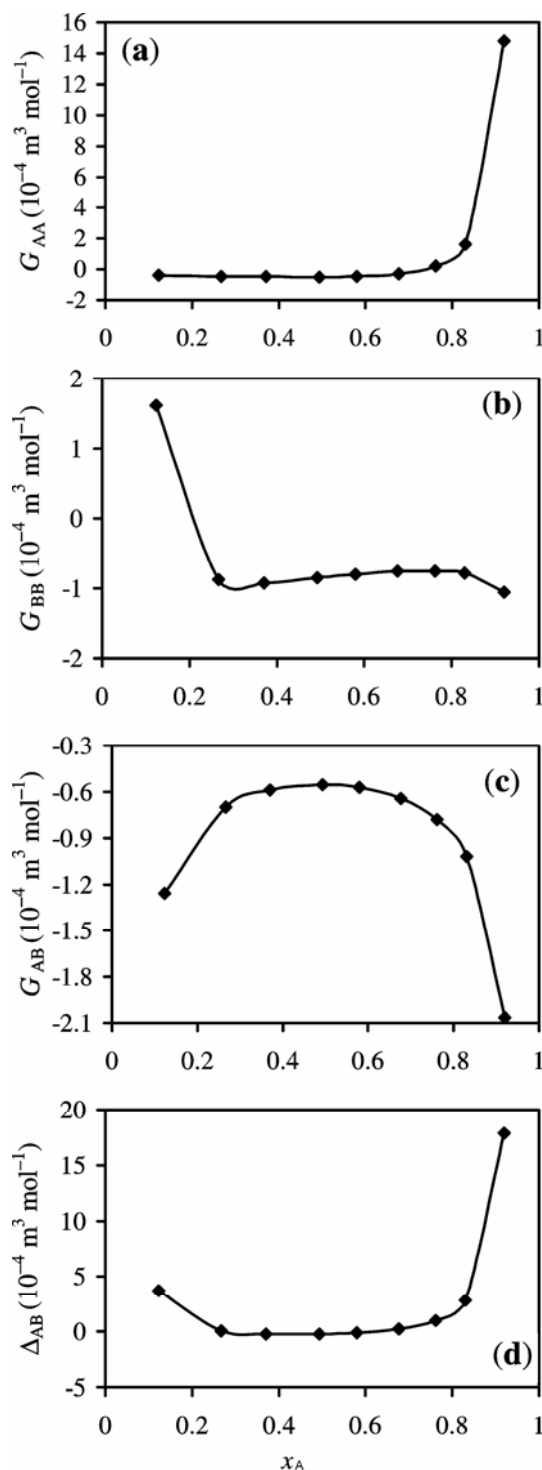


Figure 3. Plots of G_{AA} , G_{BB} , G_{AB} and Δ_{AB} against mole fraction, x_A of ACN for ACN + NMA mixtures at 298.15 K.

Figure 1(a) shows the behaviour of ACN-ACN affinity over the entire composition range. Table 2 and figure 1(a) indicate that G_{AA} values are negative and initially decreases with increase in mole fraction up to $x_A \approx 0.55$ and then increases after this point and finally become positive, suggesting decreasing correlation between ACN molecules and this correla-

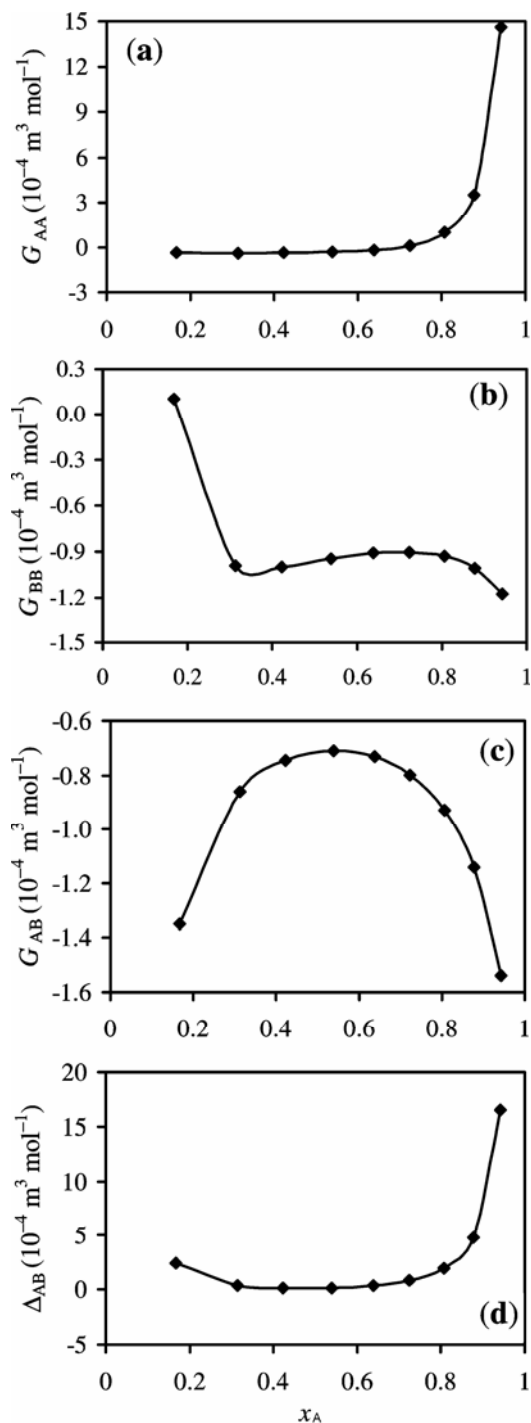


Figure 4. Plots of G_{AA} , G_{BB} , G_{AB} and Δ_{AB} against mole fraction, x_A of ACN for ACN + DMA mixtures at 298.15 K.

tion increases after $x_A \approx 0.55$ may be due to strong dipole–dipole interactions between ACN molecules at higher ACN concentration. Figure 1(b) indicates that G_{BB} values are positive and initially decrease to negative values with increase in mole fraction till $x_A \approx 0.22$ and then increases slightly after this point, suggesting decreasing correlation between FA molecules on increasing the amount of added ACN in the mixture, which leads to breaking of the associations present between FA molecules. Figure 1(c) indicates that G_{AB} values are negative and increases initially and exhibit a maximum at $x_A \approx 0.42$ and then decrease with increase in mole fraction of ACN, suggesting increasing correlation between ACN and FA molecules on increasing the amount of ACN in the mixture till $x_A \approx 0.42$, which then decreases with further increase in mole fraction of ACN. This behaviour is in agreement with the conclusions drawn in our earlier study,^{29,30} wherein V_m^E and Δk_s vs x_A curves exhibit a minimum at $x_A \approx 0.42$, indicating maximum interaction between ACN and FA molecules near this composition. Also, Δ_{AB} values (figure 1(d)) are positive and decrease initially to negative values exhibiting a minimum at $x_A \approx 0.42$ and then again increase to positive values, indicating the dissimilarity between the unlike molecules in the mixtures and negative deviations from the ideal behaviour.¹⁴

Figures 2–4 also depict similar trends in G_{AA} , G_{BB} , G_{AB} and Δ_{AB} values against mole fraction, x_A for ACN + DMF/NMA/DMA mixtures as shown by ACN + FA mixtures. A close perusal of table 2 indicates that the magnitude of G_{AB} varies in the order: FA > NMA > DMA > DMF, suggesting that the affinity or interactions between the ACN and amide molecules follow the order: FA > NMA > DMA > DMF, which is in agreement with the conclusions drawn regarding the intermolecular interactions from the trends exhibited by the excess functions of these mixtures.^{29,30}

The work on extending this procedure for calculation of K–B integrals to a variety of other binary mixture containing combination of nonpolar–nonpolar, polar–nonpolar and polar–polar liquids is in progress. We feel that in future this method may prove to be a valuable tool for the calculation of K–B integrals for all mixtures, in general.

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References

1. Iloukhani H, Zoorasna Z and Soleimani R 2005 *Phys. Chem. Liq.* **43** 391
2. George J and Sastry N V 2004 *Fluid Phase Equilib.* **216** 307
3. Giner B, Artigas H, Carrion A, Lafuente C and Royo F M 2003 *J. Mol. Liq.* **108** 303
4. Nain A K 2006 *J. Solution Chem.* **35** 1417
5. Nain A K 2007 *Phys. Chem. Liq.* **45** 371
6. Nain A K 2007 *J. Chem. Thermodyn.* **39** 462
7. Nain A K 2008 *J. Mol. Liq.* **140** 108
8. Nain A K 2008 *Fluid Phase Equilib.* **265** 46
9. Ali A, Nain A K, Chand D and Ahmad R 2006 *Bull. Chem. Soc. Jpn.* **79** 702
10. Ali A and Nain A K 2002 *Bull. Chem. Soc. Jpn.* **75** 681
11. Oswal S L, Maisuria M M and Gardas R L 2003 *J. Mol. Liq.* **108** 199
12. Gonzalez J A, Riesco N, Mozo I, De La Fuente I G and Cobos J C 2007 *Ind. Eng. Chem. Res.* **46** 1350
13. Kirkwood J G and Buff F P 1951 *J. Chem. Phys.* **19** 774
14. Ben-Naim A 1977 *J. Chem. Phys.* **67** 4884
15. Shuglin I L and Ruckenstein E 2006 *J. Phys. Chem.* **B110** 12707
16. Perera A, Sokolic F, Almasy L and Koga Y 2006 *J. Chem. Phys.* **124** 124575-1
17. Gonzalez J A, Mozo I, Villa S, Riesco N, De La Fuente, I G and Cobos J C 2006 *J. Solution Chem.* **35** 787
18. Donkersloot M C A 1979 *J. Solution Chem.* **8** 293
19. Newman K E 1994 *Chem. Soc. Rev.* **23** 31
20. Newman K E 1988 *J. Chem. Soc., Faraday Trans.* **84** 3885
21. Vergara A, Paduano L, Capuano F and Sartorio R 2002 *Phys. Chem. Chem. Phys.* **4** 4716
22. Roux A H and Desnoyers J E 1987 *Proc. Indian Acad. Sci. (Chem. Sci.)* **98** 435
23. Banerjee D, Laha A K, Chatterjee P and Bagchi S 1995 *J. Solution Chem.* **24** 301
24. Covington A K and Newman K E 1988 *J. Chem. Soc., Faraday Trans.* **84** 1393
25. Pandey J D and Verma R 2001 *Chem. Phys.* **270** 429
26. Guha A and Ghosh N K 2006 *Indian J. Chem.* **A45** 593
27. Matteoli E 1997 *J. Phys. Chem.* **B101** 9800
28. Marcus Y 2006 *J. Solution Chem.* **35** 251
29. Nain A K 2006 *Bull. Chem. Soc. Jpn.* **79** 1688
30. Nain A K 2006 *J. Chem. Thermodyn.* **38** 1362
31. Hildebrand J H and Scott R L 1962 *Regular solutions* (New Jersey: Prentice Hall)
32. Hildebrand J H 1947 *J. Chem. Phys.* **15** 225
33. Dack M R J 1975 *Chem. Soc. Rev.* **4** 211
34. Pal A and Kumar H 2004 *Indian J. Chem.* **A43** 28