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Volumetric properties of the isopropanolamine–water mixture at atmospheric pressure from 283.15 to 353.15 K

Salim Mokraoui, Alain Valtz, Christophe Coquelet, Dominique Richon *

Laboratoire de thermodynamique des équilibres entre phases, Centre Energétique et Procédés, Ecole Nationale Supérieure des Mines de paris CEP/TEP, CNRS FRE 2861, 35, Rue Saint Honoré, 77305 Fontainebleau, France

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Abstract

Densities of the isopropanolamine–water binary mixture system were measured over the whole range of compositions at temperatures from 283.15 to 353.15 K using an Anton Paar digital vibrating glass tube densimeter. The density of this system has been found an increasing function of the isopropanolamine composition. Excess molar volume data, calculated from the measured experimental densities, have been correlated using the Redlich–Kister equation. Parameters for the Redlich–Kister equation have been adjusted. Partial molar volumes at infinite dilution have been calculated for each component.

Keywords: Binary system; Isopropanolamine; Density; Excess molar volume; Partial molar volume

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1. Introduction

Isopropanolamine (IPA) could be used in carbon dioxide and hydrogen sulphide removal processes. But in order to be able to design optimized acid gas treatment equipment with this solvent, industry needs reliable physicochemical data.

The main required data are: solubility data, kinetic data, and additionally: density, viscosity, etc. In this paper, we are concerned with densities of aqueous IPA mixtures as density data seem to be missing in literature.

Densities have been measured using a vibrating tube densimeter in the (283.15–353.15 K) temperature range for the whole composition range.

Mixing of compounds gives rise to solutions with non-ideal behaviors. Deviations from ideality can be expressed through many thermodynamic functions, particularly excess or residual functions. Excess thermodynamic properties of mixtures correspond to the difference between the real and the ideal property; they provide information concerning study of molecular interactions and structure. In particular, they reflect the interactions that take place between solute–solute, solute–solvent, and solvent–solvent species. In general, positive excess molar volumes may be due to competition between strong interactions (such as those present in alcohols) and equally strong unlike H-bond interactions (such as those present between alcohols and ether). Negative excess molar volumes generally occur when unlike interactions prevail over self-association.

2. Experimental

Isopropanolamine [$H_2NC_3H_6OH$: CAS 78-96-6] was purchased from Aldrich with a certified GC purity >99%. Water [H_2O] used is ultra pure water directly prepared in our laboratory using commercial equipment (Millipore, model: direct Q5). IPA and H_2O were carefully degassed before use. The apparatus used in this work is an Anton Paar digital vibrating glass tube densimeter (model DMA5000), with a certified precision of 10^{-5} g cm^{-3}. The following relationship holds for the period of vibration, τ, and the density, ρ:

$$\rho = a + b\tau^2 \quad (1)$$

The DMA5000 was calibrated at 293.15 K (for the determination of a and b constants) with bidistilled and degassed water, and dry air. The sample density was measured at thermal equilibrium after successive increases of temperature. The temperature

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* Corresponding author. Tel.: +33 1 6469 4965; fax: +33 1 6469 4968.
E-mail address: Dominique.richon@ensmp.fr (D. Richon).

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Nomenclature

A, B, C	Parameters in Eq. (2)
A_n	Redlich–Kister parameters ($\mathrm{cm^3\,mol^{-1}}$)
m	Mass (g)
M_i	Molar mass of pure component i ($\mathrm{g\,mol^{-1}}$)
N_{exp}	Number of experimental data
p	Number of parameters of A_n
P	Pressure (Pa)
T	Temperature (K)
v_i^*	Molar volume of pure component i ($\mathrm{cm^3\,mol^{-1}}$)
$\overline{v}_i$	Partial molar volume of component i ($\mathrm{cm^3\,mol^{-1}}$)
x_i	Liquid mole fraction of component i

Greek letters

ρ	Density ($\mathrm{g\,cm^{-3}}$)
σ	Standard deviation, see Eq. (6)
∞	Infinite dilution state

Subscripts

C	Critical property
cal	Calculated property, Eq. (3)
1	IPA
2	H_2O

Superscripts

E	Excess property
*	Pure compound property

was determined with a platinum resistance with an accuracy of 0.01 K.

For preparation of mixtures, we have applied the following procedure. 20 $\mathrm{cm^3}$ glass bottles are air-tight closed with a septum and then evacuated with the help of a vacuum pump using a syringe needle introduced through the septum. Empty bottle is weighed, and then the less volatile component, freshly degassed through vacuum distillation, is introduced by means of a syringe. After weighing the bottle containing the first component, the second component is added and then the bottle is weighed again. All weighing are performed using a balance with an accuracy of 0.0001 g, therefore the average error in mole fraction (Δx_i) is estimated to be better than 0.0003 through the error equation:

$$\frac{\Delta x_i}{x_i} \le \sum_{1}^{2} \frac{\Delta m_j}{m_j} + \frac{\Delta m_i}{m_i},$$

where m_i is the weight of the component i and $\Delta m_i = 0.0003$ g is the accuracy of the balance. Loading of pure compounds and mixtures into the vibrating tube is achieved using a syringe with special care not introducing air bubbles and achieving satisfactory purging.

The above described preparation and loading procedure were used not only in order to get accurate compositions, but also to prevent from formation of gas bubbles inside the vibrating tube; this happens frequently at the highest temperatures if the liquid is not well degassed. Maximum error on v^E is estimated to be less than 0.005 $\mathrm{cm^3\,mol^{-1}}$.

Table 1
Critical temperature for IPA and parameters of Eq. (2)

T_C (K)[a]	A ($\mathrm{kmol\,m^{-3}}$)	B	C
614.0	0.8220[b]	0.2314[b]	0.2053[b]
614.0	0.8321[a]	0.2313[a]	0.2201[a]

[a] Values from Daubert et al. [2].
[b] Values obtained from our experimental data.

3. Results

Calibration of the apparatus was done with air and water. Data from Ref. [1] are suggested as a reference by Anton Paar. So, these data are also used to calculate the excess molar volume. Finally, no correlations were used in the calculation of excess molar volumes: The experimental data are directly used in order to obtain the best accuracy.

Densities of the pure IPA have been studied and compared to the values obtained with the correlation (Eq. (2)) given by Daubert et al. [2]:

$$\rho^*_{i,\mathrm{cor}} = \frac{A}{B^{(1+(1-(T/T_C))^C)}} \times \frac{M_i}{1000} \qquad (2)$$

The A, B and C parameters are presented In Table 1. Experimental densities of pure IPA are presented in Table 2. The relative deviations (see Fig. 1) between our experimental IPA densities and those calculated from Eq. (2) using the parameters from Table 1 are in general less than 0.3%. In order to improve the representation, new A, B and C parameters were fitted from our experimental data. The relative deviations between IPA experimental densities and those calculated with Eq. (2) and our parameters are smaller than 0.015%.

Densities of the mixture are reported in Table 3. Data for three isotherms (283.15, 318.15, and 353.15 K) are plotted in Fig. 2.

Excess molar volumes (see Table 3) are calculated using Eq. (3):

$$v^E = v - x_1 v_1^* - x_2 v_2^* \qquad (3)$$

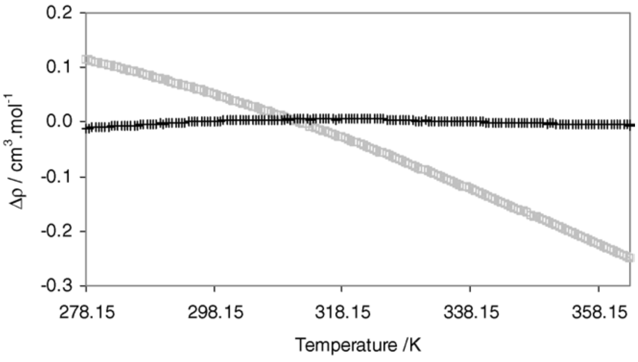

Fig. 1. Relative deviations of IPA densities. □, relative deviation between experimental data and those from correlation using the parameters of Daubert et al. [2]; +, relative deviation between experimental data and those from the correlation using our adjusted parameters.

Table 2
Density of pure IPA as a function of temperature

T (K)	ρ (g cm^{-3})	ρ_{cor} (g cm^{-3})	T (K)	ρ (g cm^{-3})	ρ_{cor} (g cm^{-3})	T (K)	ρ (g cm^{-3})	ρ_{cor} (g cm^{-3})	T (K)	ρ (g cm^{-3})	ρ_{cor} (g cm^{-3})
278.16	0.97217	0.97202	299.64	0.95520	0.95523	321.15	0.93772	0.93780	342.66	0.91966	0.91965
278.65	0.97179	0.97165	300.14	0.95480	0.95484	321.65	0.93731	0.93738	343.16	0.91923	0.91922
279.14	0.97140	0.97127	300.64	0.95440	0.95444	322.15	0.93690	0.93697	343.66	0.9188	0.91879
279.65	0.97101	0.97088	301.15	0.95400	0.95403	322.65	0.93649	0.93655	344.16	0.91837	0.91836
280.15	0.97062	0.97049	301.65	0.95359	0.95363	323.15	0.93608	0.93614	344.66	0.91794	0.91793
280.65	0.97023	0.97011	302.14	0.9532	0.95324	323.65	0.93566	0.93572	345.16	0.91751	0.91750
281.15	0.96984	0.96972	302.65	0.95279	0.95283	324.15	0.93525	0.93531	345.66	0.91708	0.91706
281.65	0.96945	0.96934	303.15	0.95239	0.95243	324.65	0.93483	0.93489	346.16	0.91665	0.91663
282.15	0.96905	0.96895	303.64	0.95199	0.95204	325.15	0.93442	0.93448	346.66	0.91621	0.91620
282.65	0.96866	0.96856	304.15	0.95159	0.95163	325.65	0.93401	0.93406	347.16	0.91578	0.91576
283.15	0.96827	0.96818	304.65	0.95118	0.95123	326.15	0.93359	0.93364	347.66	0.91535	0.91533
283.65	0.96788	0.96779	305.15	0.95078	0.95083	326.65	0.93318	0.93323	348.16	0.91492	0.91489
284.15	0.96749	0.96740	305.64	0.95038	0.95044	327.15	0.93276	0.93281	348.66	0.91448	0.91446
284.65	0.96710	0.96701	306.15	0.94998	0.95003	327.65	0.93235	0.93239	349.16	0.91405	0.91402
285.15	0.96670	0.96662	306.65	0.94957	0.94962	328.15	0.93193	0.93197	349.66	0.91361	0.91358
285.65	0.96631	0.96624	307.15	0.94917	0.94922	328.66	0.93151	0.93155	350.16	0.91318	0.91315
286.15	0.96592	0.96585	307.64	0.94877	0.94882	329.15	0.93109	0.93113	350.66	0.91274	0.91271
286.64	0.96552	0.96547	308.15	0.94836	0.94841	329.66	0.93068	0.93071	351.16	0.9123	0.91227
287.15	0.96513	0.96507	308.65	0.94795	0.94801	330.16	0.93026	0.93029	351.66	0.91187	0.91183
287.65	0.96473	0.96468	309.15	0.94755	0.94761	330.66	0.92984	0.92987	352.16	0.91143	0.91140
288.15	0.96434	0.96429	309.65	0.94714	0.94720	331.15	0.92942	0.92945	352.66	0.91099	0.91096
288.65	0.96395	0.96390	310.15	0.94674	0.94680	331.66	0.92900	0.92902	353.16	0.91055	0.91052
289.15	0.96355	0.96351	310.65	0.94633	0.94639	332.16	0.92858	0.92860	353.66	0.91012	0.91008
289.65	0.96315	0.96312	311.15	0.94592	0.94598	332.66	0.92816	0.92818	354.16	0.90968	0.90964
290.15	0.96276	0.96272	311.64	0.94552	0.94559	333.16	0.92774	0.92776	354.66	0.90923	0.90919
290.65	0.96236	0.96233	312.15	0.94511	0.94517	333.66	0.92731	0.92734	355.16	0.9088	0.90875
291.15	0.96197	0.96194	312.64	0.9447	0.94477	334.16	0.92689	0.92691	355.66	0.90835	0.90831
291.64	0.96157	0.96156	313.15	0.94430	0.94436	334.66	0.92647	0.92649	356.16	0.90791	0.90787
292.15	0.96118	0.96116	313.65	0.94389	0.94392	335.16	0.92605	0.92606	356.66	0.90747	0.90743
292.65	0.96078	0.96076	314.15	0.94348	0.94354	335.66	0.92563	0.92564	357.16	0.90703	0.90698
293.15	0.96038	0.96037	314.65	0.94307	0.94314	336.16	0.92520	0.92522	357.66	0.90659	0.90654
293.64	0.95999	0.95998	315.15	0.94266	0.94273	336.66	0.92478	0.92479	358.16	0.90614	0.90609
294.14	0.95959	0.95959	315.65	0.94225	0.94232	337.16	0.92436	0.92436	358.66	0.9057	0.90565
294.64	0.95919	0.95920	316.15	0.94184	0.94191	337.66	0.92393	0.92394	359.16	0.90526	0.90520
295.15	0.95879	0.95879	316.65	0.94143	0.94150	338.16	0.92350	0.92351	359.66	0.90481	0.90476
295.65	0.95839	0.95840	317.15	0.94103	0.94109	338.66	0.92308	0.92309	360.16	0.90436	0.90431
296.15	0.95799	0.95800	317.65	0.94061	0.94068	339.16	0.92265	0.92266	360.65	0.90392	0.90388
296.65	0.95760	0.95761	318.15	0.94020	0.94027	339.66	0.92223	0.92223	361.16	0.90347	0.90342
297.15	0.95720	0.95721	318.65	0.93979	0.93986	340.16	0.92180	0.92180	361.66	0.90303	0.90297
297.64	0.95680	0.95682	319.14	0.93938	0.93945	340.66	0.92138	0.92137	362.16	0.90258	0.90252
298.15	0.95640	0.95642	319.65	0.93896	0.93903	341.16	0.92095	0.92094	362.66	0.90213	0.90208
298.65	0.95600	0.95602	320.15	0.93855	0.93862	341.66	0.92052	0.92051	363.15	0.90168	0.90164
299.15	0.95560	0.95562	320.64	0.93814	0.93822	342.16	0.92009	0.92008	363.16	0.90169	0.90163

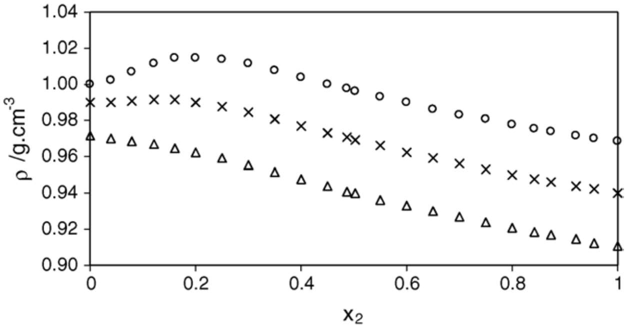

Fig. 2. Densities of IPA (1) + H_2O (2) at 283.15 K (◯), 318.15 K (×), and 353.15 K (△).

where v is the molar volume of the IPA (1) + H_2O (2) mixture, v_1^* and v_2^* are the molar volumes of the pure components.

By introducing the density ρ, Eq. (3) can be written as:

$$v^{\mathrm{E}} = \left[\frac{x_1 M_1 + x_2 M_2}{\rho}\right] - \frac{x_1 M_1}{\rho_1^*} - \frac{x_2 M_2}{\rho_2^*} \tag{4}$$

where M_1 and M_2 are respectively the molar mass of IPA and H_2O, ρ_1^* are experimental data from Table 2, ρ_2^* are from Tables produced by Bettin and Spieweck [1].

Redlich–Kister [3] equation was applied for the excess molar volume:

$$v^E = x_1 x_2 \sum_i A_i (x_1 - x_2)^i \tag{5}$$

with $i \leq 5$.

Table 3
Densities (ρ) and molar excess volumes (v^E) for IPA (1) + H_2O (2) binary mixture as a function of composition at various temperatures

x_2	T = 283.15 K		T = 288.15 K		T = 293.15 K		T = 298.15 K		T = 303.15 K	
	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})
0.0438	0.97022	−0.125	0.96631	−0.125	0.96238	−0.126	0.95841	−0.126	0.95442	−0.126
0.0801	0.97177	−0.216	0.96787	−0.215	0.96394	−0.214	0.95999	−0.214	0.95601	−0.215
0.1269	0.97408	−0.344	0.97022	−0.344	0.96631	−0.343	0.96238	−0.343	0.95841	−0.343
0.1584	0.97552	−0.414	0.97166	−0.413	0.96777	−0.413	0.96384	−0.412	0.95989	−0.412
0.2003	0.97767	−0.515	0.97382	−0.513	0.96994	−0.511	0.96603	−0.510	0.96209	−0.509
0.2999	0.98338	−0.745	0.97958	−0.741	0.97573	−0.737	0.97185	−0.734	0.96794	−0.732
0.3498	0.98651	−0.848	0.98272	−0.842	0.97889	−0.837	0.97502	−0.832	0.97112	−0.829
0.3999	0.98963	−0.931	0.98584	−0.922	0.98202	−0.915	0.97816	−0.909	0.97427	−0.904
0.4499	0.99304	−1.010	0.98926	−0.999	0.98545	−0.989	0.98159	−0.981	0.97771	−0.974
0.4968	0.99640	−1.072	0.99266	−1.060	0.98885	−1.048	0.98500	−1.038	0.98112	−1.029
0.5122	0.99762	−1.094	0.99386	−1.080	0.99005	−1.067	0.98621	−1.056	0.98233	−1.047
0.5501	1.00030	−1.123	0.99655	−1.107	0.99274	−1.092	0.98889	−1.079	0.98501	−1.068
0.6001	1.00418	−1.158	1.00045	−1.139	0.99665	−1.121	0.99281	−1.106	0.98893	−1.092
0.6501	1.00783	−1.160	1.00409	−1.137	1.00030	−1.117	0.99647	−1.098	0.99261	−1.082
0.7000	1.01117	−1.130	1.00746	−1.105	1.00371	−1.082	0.99992	−1.062	0.99609	−1.044
0.7501	1.01381	−1.059	1.01020	−1.032	1.00654	−1.008	1.00284	−0.987	0.99910	−0.968
0.8000	1.01493	−0.930	1.01154	−0.904	1.00808	−0.882	1.00458	−0.862	1.00102	−0.844
0.8400	1.01428	−0.781	1.01122	−0.759	1.00808	−0.741	1.00486	−0.724	1.00158	−0.710
0.8800	1.01159	−0.585	1.00904	−0.570	1.00638	−0.558	1.00361	−0.547	1.00073	−0.538
0.9200	1.00729	−0.365	1.00541	−0.359	1.00337	−0.354	1.00117	−0.349	0.99883	−0.346
0.9600	1.00239	−0.152	1.00124	−0.152	0.99986	−0.152	0.99826	−0.153	0.99647	−0.154
	T = 308.15 K		T = 313.15 K		T = 318.15 K		T = 323.15 K		T = 328.15 K	
	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})
0.0438	0.95039	−0.125	0.94634	−0.125	0.94226	−0.126	0.93815	−0.127	0.93400	−0.126
0.0801	0.95200	−0.214	0.94796	−0.215	0.94389	−0.216	0.93979	−0.216	0.93565	−0.216
0.1269	0.95442	−0.344	0.95039	−0.344	0.94633	−0.345	0.94224	−0.346	0.93811	−0.346
0.1584	0.95590	−0.411	0.95188	−0.411	0.94783	−0.412	0.94375	−0.413	0.93962	−0.413
0.2003	0.95811	−0.508	0.95410	−0.508	0.95006	−0.509	0.94598	−0.509	0.94187	−0.510
0.2999	0.96399	−0.730	0.96000	−0.728	0.95598	−0.728	0.95192	−0.727	0.94782	−0.727
0.3498	0.96718	−0.826	0.96321	−0.824	0.95919	−0.823	0.95513	−0.821	0.95103	−0.819
0.3999	0.97034	−0.900	0.96636	−0.895	0.96235	−0.893	0.95830	−0.890	0.95421	−0.888
0.4499	0.97378	−0.968	0.96981	−0.962	0.96580	−0.958	0.96175	−0.954	0.95765	−0.950
0.4968	0.97719	−1.021	0.97323	−1.014	0.96922	−1.008	0.96517	−1.002	0.96107	−0.997
0.5122	0.97840	−1.038	0.97444	−1.030	0.97043	−1.024	0.96638	−1.018	0.96228	−1.012
0.5501	0.98109	−1.057	0.97712	−1.048	0.97311	−1.040	0.96905	−1.032	0.96495	−1.025
0.6001	0.98501	−1.079	0.98105	−1.068	0.97704	−1.057	0.97299	−1.048	0.96889	−1.039
0.6501	0.98870	−1.067	0.98475	−1.054	0.98076	−1.042	0.97672	−1.031	0.97263	−1.021
0.7000	0.99222	−1.027	0.98830	−1.012	0.98434	−0.999	0.98034	−0.987	0.97628	−0.975
0.7501	0.99531	−0.951	0.99148	−0.936	0.98760	−0.922	0.98367	−0.909	0.97968	−0.898
0.8000	0.99741	−0.828	0.99374	−0.814	0.99002	−0.801	0.98623	−0.789	0.98239	−0.779
0.8400	0.99822	−0.697	0.99479	−0.685	0.99129	−0.675	0.98771	−0.666	0.98406	−0.658
0.8800	0.99776	−0.530	0.99467	−0.523	0.99150	−0.517	0.98822	−0.511	0.98485	−0.506
0.9200	0.99633	−0.344	0.99370	−0.341	0.99094	−0.340	0.98805	−0.338	0.98504	−0.337
0.9600	0.99449	−0.155	0.99233	−0.156	0.99001	−0.157	0.98753	−0.158	0.98491	−0.160
	T = 333.15 K		T = 338.15 K		T = 343.15 K		T = 348.15 K		T = 353.15 K	
	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})
0.0438	0.92982	−0.127	0.92559	−0.128	0.92133	−0.129	0.91702	−0.129	0.91266	−0.130
0.0801	0.93147	−0.217	0.92726	−0.219	0.92300	−0.219	0.91870	−0.220	0.91434	−0.221
0.1269	0.93395	−0.347	0.92974	−0.349	0.92548	−0.350	0.92119	−0.351	0.91684	−0.353
0.1584	0.93546	−0.414	0.93125	−0.416	0.92700	−0.417	0.92271	−0.418	0.91836	−0.420
0.2003	0.93770	−0.510	0.93351	−0.512	0.92926	−0.513	0.92497	−0.514	0.92063	−0.516
0.2999	0.94367	−0.727	0.93948	−0.728	0.93523	−0.727	0.93093	−0.727	0.92659	−0.729
0.3498	0.94688	−0.818	0.94269	−0.818	0.93845	−0.818	0.93415	−0.817	0.92981	−0.818
0.3999	0.95006	−0.886	0.94587	−0.885	0.94162	−0.883	0.93732	−0.882	0.93297	−0.881

Table 3 (*Continued*)

	$T = 333.15$ K		$T = 338.15$ K		$T = 343.15$ K		$T = 348.15$ K		$T = 353.15$ K	
	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})	ρ (g cm^{-3})	v^E (cm^3 mol^{-1})
0.4499	0.95350	−0.947	0.94931	−0.944	0.94506	−0.942	0.94076	−0.939	0.93640	−0.938
0.4968	0.95692	−0.992	0.95272	−0.989	0.94847	−0.985	0.94416	−0.981	0.93980	−0.978
0.5122	0.95813	−1.007	0.95393	−1.003	0.94968	−0.999	0.94537	−0.995	0.94101	−0.992
0.5501	0.96080	−1.018	0.95660	−1.013	0.95234	−1.008	0.94803	−1.002	0.94366	−0.998
0.6001	0.96474	−1.031	0.96054	−1.025	0.95629	−1.018	0.95198	−1.012	0.94761	−1.006
0.6501	0.96849	−1.011	0.96430	−1.003	0.96006	−0.995	0.95576	−0.988	0.95140	−0.981
0.7000	0.97217	−0.965	0.96801	−0.955	0.96380	−0.947	0.95953	−0.939	0.95520	−0.931
0.7501	0.97564	−0.887	0.97155	−0.878	0.96740	−0.869	0.96319	−0.860	0.95892	−0.853
0.8000	0.97848	−0.769	0.97451	−0.760	0.97048	−0.752	0.96638	−0.745	0.96222	−0.738
0.8400	0.98033	−0.650	0.97653	−0.643	0.97266	−0.637	0.96872	−0.631	0.96471	−0.627
0.8800	0.98139	−0.502	0.97784	−0.498	0.97420	−0.494	0.97047	−0.491	0.96666	−0.488
0.9200	0.98192	−0.336	0.97868	−0.335	0.97533	−0.334	0.97188	−0.333	0.96833	−0.333
0.9600	0.98214	−0.161	0.97924	−0.162	0.97622	−0.163	0.97307	−0.164	0.96981	−0.165

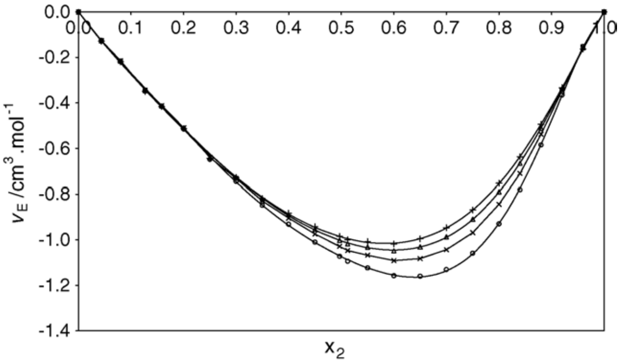

Fig. 3. Excess molar volume (v^E) for the IPA (1) + H_2O (2) binary system as a function of composition at various temperatures. ○, 283.15 K; ×, 303.15 K; +, 323.15 K; △, 343.15 K. Solid curves represent the values calculated from Eq. (3) with coefficients from Table 5.

Fig. 3 presents the experimental data of the excess molar volume and the values correlated with the Redlich–Kister equation for four isotherms.

The Redlich–Kister coefficients (A_n) have been determined at each studied temperature, they are presented in Table 4 along with the standard deviation, σ, corresponding to each fit:

$$\sigma = \sqrt{\left[\sum \frac{(v^E - v^E_{cal})^2}{N_{exp} - p}\right]} \qquad (6)$$

where p is the number of coefficients (A_n).

The temperature dependency of each coefficient given in Table 4 can be represented by second order polynomials (Eqs. (7)–(12)). The Fig. 4 shows the temperature dependency of each parameter.

$$A_0(T) = -0.0000574 \times T^2 + 0.04164 \times T - 11.474 \qquad (7)$$

$$A_1(T) = -0.0000922 \times T^2 + 0.07302 \times T - 15.526 \qquad (8)$$

$$A_2(T) = -0.0002032 \times T^2 + 0.14857 \times T - 27.411 \qquad (9)$$

$$A_3(T) = -0.0001765 \times T^2 + 0.12397 \times T - 21.900 \qquad (10)$$

$$A_4(T) = -0.0002580 \times T^2 - 0.19645 \times T + 37.868 \qquad (11)$$

$$A_5(T) = -0.0003396 \times T^2 - 0.25284 \times T + 47.843 \qquad (12)$$

Table 4
Values of Redlich–Kister coefficients at each temperature

T (K)	A_0 (cm^3 mol^{-1})	A_1 (cm^3 mol^{-1})	A_2 (cm^3 mol^{-1})	A_3 (cm^3 mol^{-1})	A_4 (cm^3 mol^{-1})	A_5 (cm^3 mol^{-1})	σ (cm^3 mol^{-1})
283.15	−4.295	−2.246	−1.658	−0.999	2.951	3.535	0.004_7
288.15	−4.244	−2.142	−1.477	−0.820	2.691	3.177	0.004_6
293.15	−4.198	−2.038	−1.312	−0.708	2.441	2.899	0.004_3
298.15	−4.157	−1.946	−1.170	−0.595	2.223	2.620	0.004_1
303.15	−4.123	−1.856	−1.035	−0.514	2.008	2.383	0.003_9
308.15	−4.090	−1.775	−0.920	−0.433	1.827	2.147	0.003_8
313.15	−4.063	−1.700	−0.811	−0.373	1.650	1.950	0.003_8
318.15	−4.039	−1.625	−0.718	−0.327	1.483	1.786	0.003_7
323.15	−4.017	−1.559	−0.631	−0.278	1.333	1.621	0.003_6
328.15	−3.997	−1.493	−0.557	−0.244	1.209	1.464	0.003_6
333.15	−3.978	−1.436	−0.481	−0.207	1.072	1.327	0.003_8
338.15	−3.964	−1.376	−0.423	−0.183	0.956	1.212	0.003_7
343.15	−3.949	−1.325	−0.362	−0.163	0.842	1.107	0.003_7
348.15	−3.934	−1.280	−0.315	−0.114	0.743	0.972	0.003_7
353.15	−3.923	−1.229	−0.278	−0.091	0.657	0.856	0.003_9

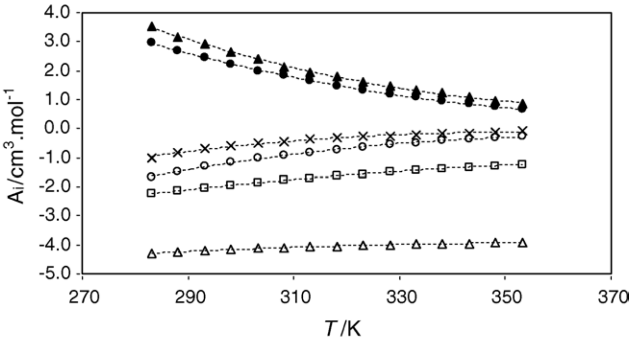

Fig. 4. Representation of the Redlich–Kister parameters, A_i as a function of T. △, A_0; □, A_1; ○, A_2; ×, A_3; ●, A_4; ▲, A_5. Dashed line: second order polynomial curve (Eqs. (7)–(12)).

The partial molar volume of each component ($\bar{v}_i$) is given by:

$$\bar{v}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j} \tag{13}$$

After differentiating Eq. (3) with respect to n_i and combining the result to Eq. (13) we obtain equations for the partial molar volume of IPA and H_2O:

$$\bar{v}_1 = v^E + v_1^* - x_2\left(\frac{\partial v^E}{\partial x_2}\right)_{T,P} \tag{14}$$

$$\bar{v}_2 = v^E + v_2^* - x_1\left(\frac{\partial v^E}{\partial x_1}\right)_{T,P} \tag{15}$$

By using the differentiation of the Redlich–Kister equation (Eq. (5)) with respect to x_2 and substitution in Eqs. (14) and (15), expressions of partial molar volumes (Eqs. (16) and (17)) are obtained:

$$\bar{v}_1 = v_1^* + x_2^2\sum A_n(1-2x_2)^n + 2x_2^2(1-x_2) \times \sum nA_n(1-2x_2)^{n-1} \tag{16}$$

$$\bar{v}_2 = v_2^* + (1-x_2)^2\sum A_n(1-2x_2)^n - 2x_2(1-x_2)^2 \times \sum nA_n(1-2x_2)^{n-1} \tag{17}$$

Interest in volumetric properties of IPA + H_2O is the determination at each temperature of the partial molar volumes of IPA at infinite dilution ($x_1 \to 0$) in H_2O and of H_2O in IPA ($x_2 \to 0$). At infinite dilution, Eqs. (16) and (17) are transformed into Eqs. (18) and (19):

$$\bar{v}_1^\infty = v_1^* + \sum A_n(-1)^n (x_1 \to 0) \tag{18}$$

$$\bar{v}_2^\infty = v_2^* + \sum A_n (x_2 \to 0) \tag{19}$$

The calculated partial molar volumes at infinite dilution and the partial molar excess volumes at infinite dilution (Eqs. (20) and (21)) are presented in Table 5.

$$(\bar{v}_1^E)^\infty = \sum A_n(-1)^n (x_1 \to 0) \tag{20}$$

$$(\bar{v}_2^E)^\infty = \sum A_n (x_2 \to 0) \tag{21}$$

4. Discussion

The excess molar volume v^E of liquid mixtures depends on the size and shape of molecules and intermolecular forces. Geometrical packing effects, free volume effects, and strong specific interactions like hydrogen bonding or dipole–dipole and dipole-induced dipole interactions, influence considerably the v^E value in a fairly complex manner. All our v^E values are negative, a characteristic of completely miscible (two polar organic molecules with the possibility of hydrogen bonding) systems. According to Table 5, the partial molar volumes at infinite dilution of IPA and water are slightly influenced by temperature. The partial molar volumes at infinite dilution of IPA ($x_1 = 0$) are smaller than the corresponding molar volumes of the pure alkanolamine, v_1^*. This could indicate that the alkanolamine molecules are partially packed inside the open or empty space left in liquid water. There is little change in the structure of liquid water. This observation is consistent with the idea that pure water has (partially) ice like

Table 5
Partial molar volumes and partial molar excess volumes at infinite dilution as a function of temperature for the IPA (1)–H_2O (2) system

T (K)	$\bar{v}_2^\infty$ (cm^3 mol^{-1})	$\bar{v}_1^\infty$ (cm^3 mol^{-1})	$(\bar{v}_2^E)^\infty$ (cm^3 mol^{-1})	$(\bar{v}_1^E)^\infty$ (cm^3 mol^{-1})
283.15	15.3_1	74.2_8	-2.7_1	-3.2_9
288.15	15.2_2	74.6_4	-2.8_1	-3.2_4
293.15	15.1_3	74.9_9	-2.9_2	-3.2_2
298.15	15.0_4	75.3_5	-3.0_3	-3.1_8
303.15	14.9_6	75.7_0	-3.1_4	-3.1_6
308.15	14.8_8	76.0_8	-3.2_5	-3.1_2
313.15	14.8_1	76.4_4	-3.3_5	-3.1_0
318.15	14.7_5	76.7_8	-3.4_4	-3.1_1
323.15	14.7_0	77.1_4	-3.5_3	-3.1_0
328.15	14.6_6	77.5_3	-3.6_2	-3.0_7
333.15	14.6_2	77.8_9	-3.7_0	-3.0_7
338.15	14.6_0	78.2_5	-3.7_8	-3.0_9
343.15	14.5_8	78.6_2	-3.8_5	-3.0_9
348.15	14.5_5	79.0_1	-3.9_3	-3.0_8
353.15	14.5_3	79.4_1	-4.0_1	-3.0_8

structure that has more free volume than packed structure of less structured liquids. Also, the partial molar volumes of water are smaller than the corresponding molar volumes of the pure water, v_2^*. This confirms the existence of hydrogen bonding which create an "empty" volume in liquid water. Moreover, v_2^∞ decreases when the temperature increases. We can imagine that the free volume increases with temperature. Hepler [4] indicates that some properties of aqueous solutions have also been interpreted in terms of the structure making or structure breaking characteristics of various solutes. This classification is based on the sign of $\left(\frac{\partial^2 \bar{v}_1^\infty}{\partial T^2}\right)_P$: a positive sign corresponds to a structure making solute while a negative sign corresponds to a structure breaking solute. According to Table 5, the first derivative $\left(\frac{\partial \bar{v}_1^\infty}{\partial T}\right)_P$ for IPA is positive. But as the different values are very close at each temperature, the second derivative is close to zero and so IPA in dilute aqueous solution can be regarded as either net structure makers or net structure breakers. This is consistent with the fact that IPA is fitting into open or empty spaces left in liquid water.

5. Conclusion

In this paper, density values of the IPA (1) + H_2O (2) were measured by the vibrating tube densimeter technique in the whole range of composition. This system is completely miscible as the values of v^E are negative. Mixture densities are represented within 0.7% in the whole range of temperatures and compositions. The partial molar volumes at infinite dilution were also determined by using the Redlich–Kister equation used to correlate the excess molar volume of the binary system.

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