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Thermodynamics of ketone + amine mixtures Part IV. Volumetric and speed of sound data at (293.15; 298.15 and 303.15 K) for 2-butanone +dipropylamine, +dibutylamine or +triethylamine systems

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ABSTRACT

Densities, ρ, and speeds of sound, u, of 2-butanone +dipropylamine, +dibutylamine or +triethylamine systems have been measured at (293.15, 298.15 and 303.15 K) and atmospheric pressure using a vibrating-tube densimeter and sound analyser Anton Paar model DSA-5000. The ρ and u values were used to calculate excess molar volumes, V^E, at the three temperatures, and the excess functions at 298.15 K for the speed of sound, u^E, the thermal expansion coefficient, α_P^E, and for the isentropic compressibility, κ_S^E. V^E, κ_S^E and α_P^E are positive magnitudes. When replacing dipropylamine by dibutylamine or triethylamine in the studied mixtures, the excess functions increase. This may be ascribed to the interactions between unlike molecules are more important in the former solutions. From the comparison with similar data obtained for propanone or 2-butanone +aniline, +*N*-methylaniline, or +pyridine systems, it is concluded that interactions between unlike molecules are stronger in mixtures containing aromatic amines. The replacement of 2-butanone by propanone in mixtures with dipropyl, dibutyl or triethylamine leads to increased V^E values, which may be explained assuming that the higher positive contribution to V^E from the disruption of the propanone–propanone interactions overcompensates the larger negative contribution related to stronger interactions between unlike molecules. Calculations in the framework of the Flory model support this conclusion. Free volume effects are present in solutions with dipropyl or dibutylamine as the V^E curves are shifted towards higher mole fractions of 2-butanone.

1. Introduction

Amides, amino acids, peptides and their derivatives are of interest because they are simple models in biochemistry. Secondary amides possess the basic (−CO) and acidic (−NH) groups of the very common, in nature, peptide bond [1]. For example, proteins are polymers of amino acids linked to each other by peptide bonds. Consequently, the understanding of liquid mixtures involving the amide functional group is necessary as a first step to a better knowledge of complex molecules of biological interest [2]. Thus, the aqueous solution of dimethylformamide is a model solvent representing the environment of the interior of proteins. In addition, amides have many other practical applications. Dimethylformamide and *N*-methylpyrrolidone are used as highly selective extractants for the recovery of aromatic and saturated hydrocarbons from petroleum feedstocks [3], and ε-caprolactam is used for the production of nylon 6, which is a polycaprolactam formed by ring-opening polymerization. The study of alkanone + amine mixtures, which contain the carbonyl and amine groups in separate molecules, is pertinent in order to gain insight into amide solutions. In this article, we report ρ, u and V^E data at (293.15, 298.15, 303.15 K), and u^E, α_P^E, and κ_S^E at 298.15 K for the mixtures 2-butanone +dipropylamine (DPA), +dibutylamine (DBA) or +triethylamine (TEA). Previously, we have provided similar data for systems containing propanone, or 2-butanone and aniline, *N*-methylaniline, or pyridine [4,5], as well as for the propanone +DPA, +DBA, or +TEA mixtures [6].

2. Experimental

2.1. Materials

2-Butanone ($\geq$0.995) and TEA ($\geq$0.995) were from Fluka, DPA ($\geq$0.99) and DBA ($\geq$0.995) were from Aldrich (purities expressed in mass fraction), and were used without further purification. The ρ and u values of the pure liquids are in good agreement with those from the literature (Table 1).

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Table 1
Physical properties of pure compounds, 2-butanone, dipropylamine, dibutylamine and triethylamine at temperature T: ρ, density; u, speed of sound; α_P, isobaric thermal expansion coefficient; κ_S, adiabatic compressibility; κ_T, isothermal compressibility and C_P, isobaric heat capacity. Reduction parameters used in the Flory model for volume, V^*, and pressure, P^*, are also included.

Property	T/K	2-Butanone		Dipropylamine		Dibutylamine		Triethylamine	
		This work	Lit	This work	Lit	This work	Lit	This work	Lit
ρ/g cm^3	293.15	0.805351	0.80495[a]	0.738188	0.73720[b]	0.759571	0.762022[c]	0.727515	0.7276[d] 0.72753[e]
	298.15	0.800077	0.7997[f] 0.79974[a,i] 0.79992[l]	0.733683	0.73336[g] 0.73368[h] 0.73333[m]	0.755457	0.75553[g] 0.75570[j] 0.75572[h] 0.75595[k]	0.722822	0.72318[h] 0.72376[k]
	303.15	0.794779	0.79464[l] 0.79448[a]	0.729087	0.72820[b] 0.73121[k] 0.73019[n]	0.751329	0.75194[k] 0.75248[n]	0.718201	0.71836[e]
u/m s^{-1}	293.15	1212.3	1213[a]	1209.2		1261.2	1269.47[c]	1132.77	
	298.15	1191.0	1192[a]	1187.7	1198[k]	1241.3	1248[k] 1246.7[c]	1111.1	1123[k] 1115.1[o]
	303.15	1170.8	1171[a]	1167.1	1174[k]	1222.5	1227[k]	1090.7	1101[k]
$10^3\ \alpha_P$/K^{-1}	298.15	1.32	1.31[a]	1.24	1.201[k]	1.09	1.059[k]	1.29	1.24[o]
κ_S/TPa^{-1}	293.15	844.9	844[a]	926.5		827.7	814.31[c]	1071.2	
	298.15	881.2	880[a]	966.2	947[k]	859.0	849[k]	1120.7	1113[o]
	303.15	917.9	918[a]	1006.9	992[k]	890.6	883[k]	1170.5	1135[k]
κ_T/TPa^{-1}	298.15	1175.9	1188[d]	1216.4	1183[k]	1060.1	1039[k]	1441.0	1404[o]
C_P/J mol^{-1} K^{-1}	298.15		159.2[p]		252.84[d]		302[k]		216.43[q]
$V^{*\,r}$/cm^3 mol^{-1}	298.15	68.80	106.51	135.15	107.33				
$P^{*\,r}$/J cm^{-3}	298.15	574.2	509.6	491.2	454.				

$V^* = 54.69$ cm^3 mol^{-1}; $P^* = 619.1$ J cm^{-3}; values obtained using α_P and κ_T from Ref. [4].

[a] [37].
[b] [38].
[c] [39].
[d] [10].
[e] [40].
[f] [41].
[g] [42].
[h] [24].
[i] [43].
[j] [44].
[k] [45].
[l] [46].
[m] [47].
[n] [48].
[o] [49].
[p] [50].
[q] [51].
[r] For propanone.

2.2. Apparatus and procedure

Binary mixtures were prepared by mass in small vessels of about 10 cm^3. Caution was taken to prevent evaporation, and the error in the final mole fraction is estimated to be less than ±0.0001. Conversion to molar quantities was based on the relative atomic mass table of 2006 issued by IUPAC [7].

The densities and speeds of sound of both pure liquids and of the mixtures were measured using a vibrating-tube densimeter and sound analyser, Anton Paar model DSA-5000, automatically thermostated within ±0.01 K. Temperature measurements were taken using a Pt-100, calibrated at the triple point of water (0.01 °C) and at the melting point of gallium (29.7646 °C) according to the ITS-90 scale [8,9]. The calibration of the densimeter was carried out with deionised double-distilled water, heptane, octane, isooctane, cyclohexane and benzene, using ρ values from the literature [10–12]. The accuracy for the ρ and u measurements are $\pm 1 \times 10^{-5}$ g cm^{-3} and ±0.1 m s^{-1}, respectively, and the corresponding precisions are $\pm 1 \times 10^{-6}$ g cm^{-3} and ±0.01 m s^{-1}. The experimental technique was checked by determining V^E and u of the standard mixtures: cyclohexane + benzene at the temperatures (293.15, 298.15 and 303.15 K) and 2-ethoxyethanol + heptane at 298.15 K. Our results agree well with published values [13–16]. The accuracy in V^E is believed to be less than $\pm(0.01\left|V^E_{\max}\right| + 0.005)$ cm^3 mol^{-1}, where $|V^E_{\max}|$ denotes the maximum experimental value of the excess molar volume with respect to the mole fraction. The accuracy of the deviations of u from the ideal behaviour is estimated to be 0.3 m s^{-1}.

3. Equations

The thermodynamic properties for which values are derived most directly from the experimental measurements are the density, ρ, the molar volume, V, the coefficient of thermal expansion, $\alpha_P = -(1/\rho)(\partial\rho/\partial T)_P$ and the isentropic compressibility, κ_S. In this work, α_P values were obtained from a linear dependence of ρ with T. Assuming that the absorption of the acoustic wave is negligible, κ_S can be calculated using the Newton–Laplace's equation:

$$\kappa_S = \frac{1}{\rho u^2} \tag{1}$$

For an ideal mixture at the same temperature and pressure than the system under study, the values F^{id} of the thermodynamic prop-

Table 2
Densities, ρ, molar excess volumes, V^E, and speeds of sound for 2-butanone(1) + amine(2) mixtures at temperature T.

x_1	$\rho/\mathrm{g\,cm^{-3}}$	$V^E/\mathrm{cm^3\,mol^{-1}}$	$u/\mathrm{m\,s^{-1}}$	x_1	$\rho/\mathrm{g\,cm^{-3}}$	$V^E/\mathrm{cm^3\,mol^{-1}}$	$u/\mathrm{m\,s^{-1}}$
2-Butanone(1) + dipropylamine(2); T/K = 293.15							
0.0539	0.740359	0.043	1208.02	0.5551	0.767388	0.139	1204.38
0.1021	0.742443	0.069	1207.27	0.6014	0.770563	0.136	1204.49
0.1497	0.744612	0.088	1206.70	0.6568	0.774567	0.128	1204.76
0.1982	0.746936	0.101	1206.17	0.6968	0.777603	0.120	1205.12
0.2459	0.749311	0.112	1205.69	0.7555	0.782275	0.107	1205.87
0.2983	0.752034	0.122	1205.17	0.8009	0.786111	0.092	1206.59
0.3504	0.754874	0.130	1204.86	0.8573	0.791158	0.068	1207.83
0.4012	0.757757	0.137	1204.58	0.9010	0.795276	0.049	1208.90
0.4495	0.760619	0.142	1204.35	0.9479	0.799908	0.027	1210.29
0.5068	0.764200	0.142	1204.30				
2-Butanone(1) + dipropylamine(2); T/K = 298.15							
0.0592	0.736042	0.050	1186.64	0.5539	0.762376	0.142	1182.71
0.1027	0.737924	0.071	1185.88	0.5992	0.765587	0.136	1183.16
0.1509	0.740108	0.087	1185.19	0.6474	0.769011	0.130	1183.43
0.2001	0.742441	0.101	1184.66	0.6987	0.772610	0.115	1183.49
0.2446	0.744623	0.114	1184.17	0.7531	0.777151	0.105	1184.56
0.2958	0.747263	0.123	1183.84	0.8048	0.781469	0.089	1185.36
0.3545	0.750410	0.134	1183.33	0.8557	0.785991	0.066	1186.62
0.4003	0.753000	0.139	1183.16	0.9041	0.790463	0.050	1188.02
0.4625	0.756591	0.145	1182.49	0.9471	0.794714	0.025	1189.12
0.5006	0.759040	0.143	1182.88				
2-Butanone(1) + dipropylamine(2); T/K = 303.15							
0.0658	0.731678	0.055	1165.92	0.5554	0.757601	0.145	1162.39
0.0988	0.733107	0.067	1165.40	0.6081	0.761161	0.139	1162.63
0.1106	0.733626	0.072	1165.23	0.6657	0.765248	0.132	1163.01
0.2146	0.738432	0.104	1164.09	0.7041	0.768129	0.124	1163.52
0.2595	0.740626	0.118	1163.49	0.7517	0.771855	0.110	1163.99
0.3098	0.743197	0.129	1163.09	0.8032	0.776094	0.094	1164.84
0.3630	0.746053	0.138	1162.78	0.8513	0.780312	0.071	1166.07
0.4131	0.748859	0.143	1162.50	0.8958	0.784355	0.055	1166.99
0.4570	0.751472	0.149	1162.37	0.9448	0.789085	0.029	1168.60
0.5154	0.755069	0.149	1162.30				
2-Butanone(1) + dibutylamine(2); T/K = 293.15							
0.0568	0.760739	0.053	1258.16	0.5553	0.776145	0.259	1231.06
0.1152	0.762014	0.105	1254.96	0.6022	0.778277	0.254	1228.89
0.1488	0.762814	0.129	1252.90	0.6554	0.780870	0.245	1225.75
0.1968	0.764024	0.158	1250.30	0.7036	0.783444	0.231	1223.35
0.2539	0.765570	0.188	1247.19	0.7554	0.786435	0.211	1220.79
0.3056	0.767093	0.209	1244.42	0.8022	0.789404	0.186	1218.72
0.3564	0.768675	0.228	1241.62	0.8598	0.793411	0.147	1216.34
0.4105	0.770501	0.243	1238.72	0.9001	0.796544	0.109	1214.96
0.4545	0.772103	0.245	1236.36	0.9513	0.800881	0.055	1213.50
0.5005	0.773872	0.256	1233.96				
2-Butanone(1) + dibutylamine(2); T/K = 298.15							
0.0681	0.756775	0.066	1237.35	0.5455	0.771147	0.267	1211.00
0.1038	0.757539	0.097	1235.31	0.6036	0.773698	0.261	1207.71
0.1625	0.758950	0.139	1232.05	0.6514	0.775963	0.253	1205.23
0.2034	0.759972	0.163	1229.94	0.7003	0.778472	0.241	1202.70
0.2603	0.761475	0.194	1226.66	0.7473	0.781050	0.226	1200.27
0.3112	0.762929	0.216	1223.83	0.7978	0.784142	0.198	1197.91
0.3523	0.764175	0.232	1221.60	0.8456	0.787356	0.164	1195.86
0.3937	0.765506	0.246	1219.44	0.9022	0.791581	0.112	1193.73
0.4420	0.767105	0.260	1216.58	0.9482	0.795385	0.064	1192.26
0.5018	0.769396	0.264	1213.32				
2-Butanone(1) + dibutylamine(2); T/K = 303.15							
0.0621	0.752548	0.055	1218.87	0.5402	0.766282	0.282	1191.57
0.1098	0.753539	0.098	1216.11	0.6005	0.768842	0.276	1188.20
0.1666	0.754759	0.151	1212.59	0.6493	0.771091	0.267	1185.58
0.2074	0.755736	0.178	1210.29	0.7004	0.773646	0.253	1182.87
0.2593	0.757080	0.205	1207.25	0.7486	0.776288	0.232	1180.45
0.3090	0.758454	0.228	1204.69	0.8005	0.779398	0.202	1177.89
0.3551	0.759790	0.250	1201.97	0.8456	0.782362	0.169	1175.94
0.4045	0.761368	0.262	1199.30	0.899	0.786254	0.122	1173.70
0.4566	0.763133	0.275	1196.39	0.953	0.790578	0.061	1171.96
0.4957	0.764551	0.280	1194.07				
2-Butanone(1) + triethylamine(2); T/K = 293.15							
0.0684	0.730666	0.066	1134.48	0.5572	0.761332	0.144	1162.26
0.1169	0.733080	0.098	1136.03	0.6100	0.765576	0.135	1166.74
0.1627	0.735417	0.132	1137.96	0.6519	0.769122	0.124	1170.56

Table 2 (*Continued*)

x_1	ρ/g cm^{-3}	V^E/cm^3 mol^{-1}	u/m s^{-1}	x_1	ρ/g cm^{-3}	V^E/cm^3 mol^{-1}	u/m s^{-1}
0.2218	0.738705	0.149	1140.60	0.7051	0.773808	0.112	1175.66
0.2686	0.741430	0.162	1142.96	0.7603	0.778962	0.097	1181.38
0.3141	0.744214	0.167	1145.52	0.8057	0.783447	0.079	1186.51
0.3549	0.746818	0.168	1147.86	0.8586	0.788929	0.061	1192.76
0.4154	0.750867	0.165	1151.74	0.9019	0.793679	0.042	1198.33
0.4636	0.754264	0.161	1155.05	0.9451	0.798586	0.028	1204.10
0.5054	0.757343	0.154	1158.17				
2-Butanone(1) + triethylamine(2); T/K = 298.15							
0.0709	0.725999	0.082	1112.73	0.5701	0.757323	0.154	1141.48
0.1149	0.728152	0.115	1114.19	0.6039	0.760048	0.145	1144.46
0.1580	0.730378	0.138	1115.89	0.6600	0.764735	0.134	1149.45
0.2181	0.733668	0.159	1118.52	0.7122	0.769362	0.119	1154.62
0.2610	0.736151	0.167	1120.74	0.7604	0.773883	0.099	1159.77
0.3203	0.739738	0.175	1123.91	0.8023	0.777983	0.084	1164.44
0.3605	0.742292	0.178	1126.28	0.8437	0.782252	0.063	1169.62
0.4159	0.745987	0.175	1129.87	0.8921	0.787444	0.042	1175.66
0.4607	0.749113	0.171	1132.99	0.9456	0.793453	0.025	1182.84
0.5106	0.752756	0.163	1136.68				
2-Butanone(1) + triethylamine(2); T/K = 303.15							
0.0686	0.721221	0.082	1092.17	0.5652	0.752023	0.159	1120.58
0.1149	0.723470	0.116	1093.65	0.6051	0.755192	0.151	1124.04
0.1643	0.726011	0.143	1095.56	0.6561	0.759446	0.137	1128.72
0.2101	0.728487	0.161	1097.57	0.7087	0.764061	0.121	1134.02
0.2639	0.731565	0.172	1100.29	0.7630	0.769188	0.107	1139.97
0.3102	0.734326	0.181	1102.73	0.7945	0.772200	0.087	1143.48
0.3502	0.736816	0.185	1105.13	0.8542	0.778238	0.062	1150.54
0.3869	0.739189	0.185	1107.37	0.8987	0.783012	0.043	1156.33
0.4500	0.743482	0.180	1111.65	0.9500	0.788818	0.021	1163.38
0.5081	0.747667	0.172	1115.97				

erty, F, are calculated using the equations [13,17]:

$$F^{\mathrm{id}} = x_1F_1 + x_2F_2 \quad (F = V; C_{\mathrm{P}}) \tag{2}$$

and

$$F^{\mathrm{id}} = \phi_1F_1 + \phi_2F_2 \quad (F = \alpha_{\mathrm{P}}; \kappa_{\mathrm{T}}) \tag{3}$$

where C_{P} is the isobaric heat capacity, $\phi_i = x_iV_i/V^{id}$ the volume fraction, κ_{T}, the isothermal compressibility, and F_i, the F value of component i, respectively. For κ_{S} and u, the ideal values are calculated according to [17]:

$$\kappa_{\mathrm{S}}^{\mathrm{id}} = \kappa_{\mathrm{T}}^{\mathrm{id}} - \frac{TV^{\mathrm{id}}\alpha_{\mathrm{P}}^{\mathrm{id2}}}{C_{\mathrm{P}}^{\mathrm{id}}} \tag{4}$$

and

$$u^{\mathrm{id}} = \left(\frac{1}{\rho^{\mathrm{id}}\kappa_{\mathrm{S}}^{\mathrm{id}}}\right)^{1/2} \tag{5}$$

where $\rho^{\mathrm{id}} = (x_1M_1 + x_2M_2)/V^{\mathrm{id}}$ (M_i, molecular mass of the i component). In this work, we have determined the excess functions:

$$F^{\mathrm{E}} = F - F^{\mathrm{id}} \tag{6}$$

4. Results and discussion

Table 2 lists values of densities, calculated V^{E} and of u vs. x_1, the mole fraction of the 2-butanone. Table 3 contains the derived quantities $\kappa_{\mathrm{S}}^{\mathrm{E}}$, $\alpha_{\mathrm{P}}^{\mathrm{E}}$ and u^{E}. The data were fitted by unweighted least-squares polynomial regression to the equation:

$$F^{\mathrm{E}} = x_1(1 - x_1)\sum_{i=0}^{k-1} A_i(2x_1 - 1)^i \tag{7}$$

where F stands for the properties cited above. The number of coefficients k used in Eq. (7) for each mixture was determined by applying an F-test [18] at the 99.5% confidence level. Table 4 lists the parameters A_i obtained in the regression, together with the standard deviations σ, defined by:

$$\sigma(F^{\mathrm{E}}) = \left[\frac{1}{N-k}\sum(F^{\mathrm{E}}_{\mathrm{cal}} - F^{\mathrm{E}}_{\mathrm{exp}})^2\right]^{1/2} \tag{8}$$

where N is the number of direct experimental values. Results on V^{E} and $\kappa_{\mathrm{S}}^{\mathrm{E}}$ are shown graphically in Figs. 1 and 2. No data have been encountered in the literature for comparison.

Hereafter, we are referring to values of the excess molar properties at equimolar composition and 298.15 K.

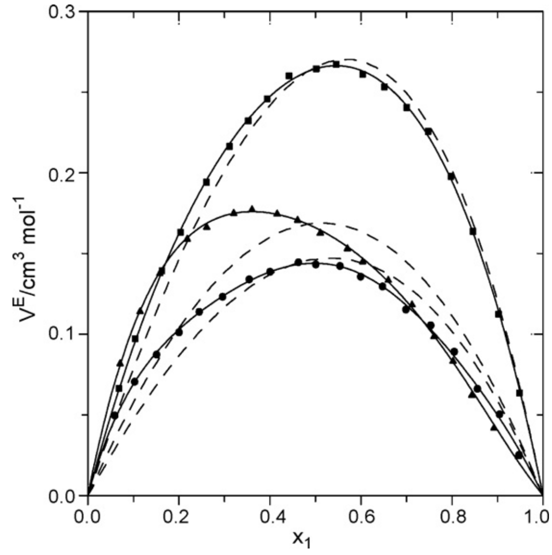

Fig. 1. V^{E} for the 2-butanone(1) + amine(2) systems at atmospheric pressure and 298.15 K. Full symbols (this work): (●), DPA; (■), DBA; (▲), TEA. Solid lines, calculations with Eq. (7) using the coefficients from Table 4. Dashed lines, results form the Flory model (see text).

Table 3
Excess functions at 298.15 K for κ_S, adiabatic compressibility, u, speed of sound, and α_P, isobaric thermal expansion coefficient of 2-butanone(1) + amine(2) mixtures.

x_1	κ_S^E/TPa^{-1}	u^E/m^{-1}	α_P^E/10^{-6} K^{-1}
2-Butanone(1) + dipropylamine(2)			
0.0592	1.89	−0.95	1.37
0.1027	3.14	−1.63	0.73
0.1509	4.26	−2.25	−0.23
0.2001	5.11	−2.71	−0.73
0.2446	5.91	−3.15	−0.48
0.2958	6.46	−3.45	0.51
0.3545	7.33	−3.94	2.25
0.4003	7.67	−4.13	3.63
0.5006	8.30	−4.52	5.35
0.5992	8.14	−4.48	4.19
0.6474	7.92	−4.39	2.86
0.7531	6.78	−3.82	0.23
0.8048	5.96	−3.39	0.07
0.8557	4.48	−2.58	0.85
0.9041	2.97	−1.69	2.19
0.9471	1.86	−1.12	2.64
2-Butanone(1) + dibutylamine(2)			
0.0681	2.90	−1.81	0.88
0.1038	4.25	−2.65	1.77
0.1625	6.18	−3.88	3.61
0.2034	7.23	−4.51	5.19
0.2603	9.09	−5.66	7.59
0.3112	10.46	−6.48	9.76
0.3523	11.41	−7.04	11.46
0.3937	12.12	−7.43	13.04
0.4420	13.39	−8.16	14.73
0.5018	14.18	−8.64	16.11
0.5455	14.55	−8.82	16.79
0.6036	15.10	−9.14	17.01
0.6515	15.01	−9.04	16.64
0.7003	14.69	−8.80	15.70
0.7473	14.17	−8.44	14.32
0.7978	12.88	−7.65	12.19
0.8456	11.08	−6.56	9.68
0.9022	8.04	−4.76	6.25
0.9482	4.81	−2.85	3.28
2-Butanone(1) + triethylamine(2)			
0.0709	2.73	−1.03	7.90
0.1149	3.67	−1.38	9.82
0.1580	4.19	−1.55	10.47
0.2181	4.62	−1.69	10.41
0.2610	4.45	−1.57	10.18
0.3203	4.40	−1.52	10.21
0.3605	4.17	−1.40	10.53
0.4159	3.63	−1.13	11.34
0.4607	3.16	−0.89	12.19
0.5106	2.60	−0.63	13.08
0.5701	1.86	−0.26	13.67
0.6039	1.31	0.01	13.56
0.6600	0.90	0.19	12.44
0.7122	0.31	0.47	10.11
0.7604	−0.28	0.73	6.88
0.8023	−0.50	0.79	3.51
0.8437	−1.12	1.07	−0.03
0.8921	−0.99	0.89	−3.42
0.9456	−0.55	0.52	−4.52

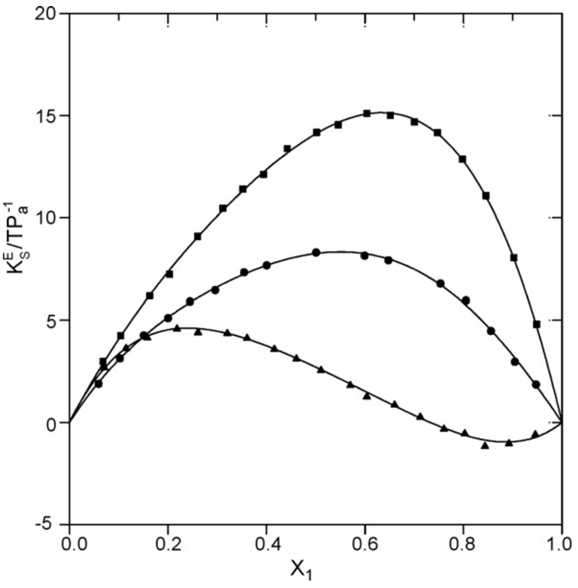

Fig. 2. κ_S^E for the for the 2-butanone(1) + amine(2) systems at atmospheric pressure and 298.15 K. Full symbols (this work): (●), DPA; (■), DBA; (▲), TEA. Solid lines, calculations with Eq. (7) using the coefficients from Table 4.

Mixtures of 2-butanone with a given alkane are characterized by strong dipolar interactions between the ketone molecules. Thus, for the heptane system, H^E and V^E values are 1338 J mol^{-1} [19] and 0.794 cm^3 mol^{-1} [20], respectively. The large positive V^E value indicates that the interactional contribution to this excess function, due to the disruption of the ketone–ketone interactions upon mixing, is much more important than those related to effects which contribute negatively to V^E (structural effects arising from interstitial accommodation of one component into the other and free volume effects). Dipropylamine and dibutylamine are secondary amines, and are weakly self-associated [21]. Accordingly, the mixtures with alkanes show relatively low H^E values: 456 J mol^{-1} for DPA + heptane [22], and 277 J mol^{-1} for DBA + heptane (at 303.15 K) [23]. The corresponding V^E values are lower than in the case of 2-butanone solutions: 0.258 cm^3 mol^{-1} (DPA + heptane) and 0.052 cm^3 mol^{-1} (DBA + heptane) [24]. The latter value suggests that structural effects may become important, which is supported by the negative V^E of the DBA + hexane system, −0.185 cm^3 mol^{-1} [24]. Such effects are also relevant in mixtures including TEA [25], a weakly polar tertiary amine. In solutions with heptane, H^E = 112 J mol^{-1} and V^E = 0.1255 cm^3 mol^{-1} [26], while in the hexadecane system, H^E = 322 J mol^{-1} [27] V^E = −0.0979 cm^3 mol^{-1} [28].

We note that for the studied mixtures, V^E is positive. Therefore, the contribution to V^E from the breaking of the interactions between like molecules upon mixing is predominant over the negative contributions from structural effects and interactions between unlike molecules. The existence of such interactions is supported by the V^E decrease observed in 2-butanone mixtures when heptane is replaced by DPA, two solvents of similar size. It is remarkable that the V^E, α_p^E and κ_S^E magnitudes are positive for propanone, or 2-butanone +DPA, +DBA or +TEA systems (Tables 2 and 3 Figs. 1–3), while they are negative quantities for propanone or 2-butanone +aniline, +*N*-methylaniline, or +pyridine [5,6]. For example, in the case of the 2-butanone + aniline and $\kappa_S^E = -113.4$ TPa^{-1}. This means that interactions between unlike molecules are much stronger in mixtures including aromatic amines. In fact, the strength of the 2-propanone–aniline interactions has been estimated to be −30.50 kJ mol^{-1} [4], a higher absolute value than that of the H-bonds between 1-alkanol molecules (−25 kJ mol^{-1}). In addition, it is known that negative $(\partial V^E/\partial T)_P$ values are encountered in systems characterized by complex formation, as amine + chloroform, and are interpreted in terms of a decrease in the molar volume of complex formation (with increasing temperature), which overcompensates for the decrease in the extent of complex formation [29,30].

The V^E increase observed when replacing DPA by DBA may be ascribed to the interactions between 2-butanone molecules are broken more easily by DBA, due to its larger aliphatic surface. Moreover, the creation of the amine–ketone interactions is more difficult as the amine group is more sterically hindered in

Table 4
Coefficients A_i and standard deviations, $\sigma(F^E)$ (Eq. (8)) for representation of the $F^{E,a}$ property at 298.15 K for 2-butanone(1) + amine(2) systems by Eq. (7).

System	T/K	Property F^E	A_0	A_1	A_2	A_3	A_4	$\sigma(F^E)$
2-Butanone + dipropylamine	293.15	V^E	0.562	0.018	0.127	−0.21		0.002
	298.15	V^E	0.576	−0.006	−0.04	−0.20	0.27	0.002
		u^E	−17.99	−4.3	−2.3	3.3		0.07
		κ_S^E	33.0	6.3	3.6	−7.4		0.11
		α_P^E	21.8	3.5	−138	7	201	0.18
	303.15	V^E	0.594	0.022	−0.03	−0.21	0.23	0.002
2-Butanone + dibutylamine	293.15	V^E	1.024	0.141	0.159			0.002
	298.15	V^E	1.058	0.168	0.161			0.002
		u^E	−34.4	−15.7	−10.3			0.06
		κ_S^E	56.43	28.2	17.9			0.11
		α_P^E	64.42	40.0	−30.5	−10.6		0.04
	303.15	V^E	1.121	0.170	0.11			0.003
2-Butanone + triethylamine	293.15	V^E	0.624	−0.318	0.218			0.002
	298.15	V^E	0.664	−0.273	0.223	−0.27		0.002
		u^E	−2.72	11.1	0.7	5.6		0.06
		κ_S^E	10.84	−22.7	4.0	−11.3		0.12
		α_P^E	52.9	35	−28	−197		0.3
	303.15	V^E	0.692	−0.296	0.205	−0.22		0.002

[a] $F^E = V^E$, units: cm^3 mol^{-1}; $F^E = u^E$, units: m s^{-1}; $F^E = \kappa_S^E$, units: TPa^{-1}; $F^E = \alpha_P^E$, units: 10^{-6} K^{-1}.

this amine. On the other hand, V^E is higher for the TEA solution than for the DPA mixture. This reveals that the interactions between unlike molecules are more important in the latter system, which is confirmed by the larger α_P^E value encountered for the TEA solution (Table 3). We note that the V^E curves are shifted to higher mole fractions of 2-butanone, the smaller component, in solutions with DPA, or DBA (Fig. 1), which is typical of systems where free volume effects are present [19]. Similar trends are found for propanone +DPA, +DBA, or +TEA mixtures. The parameter $\chi = (u/u^{id})^2 - 1$ is widely used to estimate the non-ideality of a system, [31–34] as solutions with strong deviations from the ideal behaviour are characterized by high χ values. For example, for 2-pyrrolidone mixtures, χ(methanol) = 0.8 and χ(ethanol) = 0.35 [32]. For systems with 2-butanone, χ(DPA) = −0.008; χ(DBA) = −0.014; χ(TEA) 0.001; χ(aniline) = 0198; χ(N-methylaniline) = 0.120; and χ(pyridine) = 0.070. This is in agreement with our previous findings: interactions between unlike molecules are weaker in DBA solutions, and such interactions are much stronger in those systems with aromatic amines.

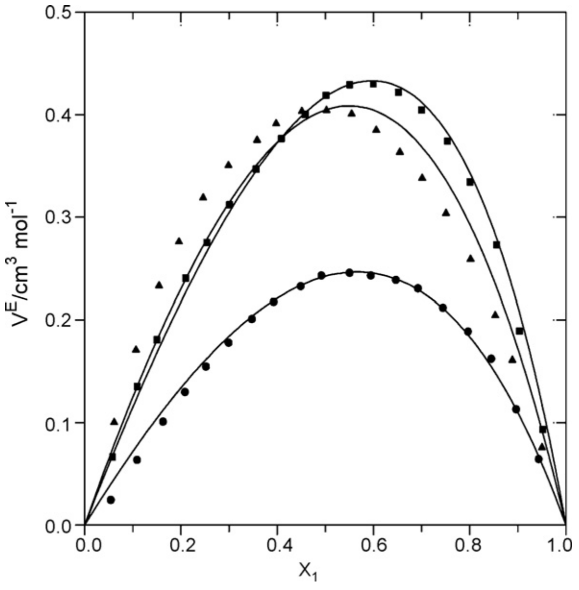

Fig. 3. V^E for the propanone(1) + amine(2) systems at atmospheric pressure and 298.15 K. Full symbols [6]: (●), DPA; (■), DBA; (▲), TEA. Solid lines, results form the Flory model (see text).

The replacement of 2-butanone by propanone in mixtures with DPA, DBA or TEA leads to increased V^E values (see Figs. 1 and 3). This may be interpreted assuming that the higher positive contribution to V^E from the disruption of the propanone–propanone interactions overcompensates the larger negative contribution related to stronger interactions between unlike molecules. On the other hand, structural effects increase with the size of the alkanone, as it is revealed by $V^E < 0$ for the 2-heptanone + TEA mixture (I. Alonso, personal communication).

Finally, we have applied the Flory model [35] to propanone or 2-butanone +DPA, +DBA, or +TEA systems. The reduction parameters for volume, V^* and for pressure, P^*, of pure substances are given in Table 1. A graphical comparison between experimental data and theoretical results is shown in Figs. 1 and 3. The model represents fairly well the V^E curves, except that of the 2-butanone + TEA mixture. Discrepancies may be due to structural effects related to the globular shape of TEA, which are also encountered in systems with 1-alkanols [36], or n-alkanes (see above). The Flory interaction parameters, X_{12}, determined in this work are (in J cm^{-3}): 6.35 (2-butanone + DPA); 9.5 (2-butanone + DBA) and 7.05 (2-butanone + TEA), and 7.75 (propanone + DPA); 14.85 (propanone + DBA) and 10.4 (propanone + TEA). This newly points out that interactions between like molecules are more relevant in propanone solutions, or in mixtures with DBA compared with those including DPA.

5. Conclusions

In this work, we have determined V^E, κ_S^E and α_P^E for 2-butanone +DPA, +DBA, or +TEA. These excess functions are positive, and increase when replacing DPA by DBA or TEA. This may be attributed to interactions between unlike molecules are more important in the DPA solution. The replacement of 2-butanone by propanone leads to increased V^E values, which may be attributed to interactions between like molecules are more relevant in propanone systems, which is confirmed by Flory calculations. Data suggest that the interactions between unlike molecules are weaker in the studied systems than in 2-butanone + aromatic amine mixtures.

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