Thermodynamics of Ketone + Amine Mixtures. Part III. Volumetric and Speed of Sound Data at (293.15, 298.15, and 303.15) K for 2-Butanone + Aniline, + *N*-Methylaniline, or + Pyridine Systems†

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Densities, ρ, and speeds of sound, u, of 2-butanone + aniline, + *N*-methylaniline, or + pyridine systems have been measured at (293.15, 298.15, and 303.15) K and atmospheric pressure using a vibrating-tube densimeter and sound analyzer (Anton Paar model DSA-5000). The ρ and u values were used to calculate excess molar volumes, V^E, and the excess functions at 298.15 K for the speed of sound, u^E, the thermal expansion coefficient, α_P^E, and the isentropic compressibility, κ_S^E. V^E and κ_S^E are both negative magnitudes and increase in the sequence: aniline < *N*-methylaniline < pyridine. In contrast, u^E is positive and changes in the opposite way. Data suggest the existence of strong interactions between unlike molecules.

Introduction

It is known that peptide bonds are very common in nature.[1] So, proteins are polymers of amino acids linked to each other by such bonds. This makes the study of amides, amino acids, peptides, and their derivatives very interesting, as they are simple models in biochemistry. For example, the aqueous solution of dimethylformamide is a model solvent representing the environment of the interior of proteins. 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] Because the amide group may be considered to be built by the carbonyl group and the amine group ($-NH_2$, >NH, >N−), the study of alkanone + amine mixtures, which contain the carbonyl and amine groups in separate molecules, is pertinent to gain insight into amide solutions. In this work, we report densities, speeds of sound, and excess molar volumes at (293.15, 298.15, and 303.15) K and κ_S^E, u^E, and α_P^E at 298.15 K for 2-butanone + aniline, + *N*-methylaniline, or + pyridine mixtures. Previously, we have provided this type of data for systems including 2-propanone and the same aromatic amines[3] or for 2-propanone + dipropylamine, + dibutylamine, or + triethylamine mixtures.[4]

Experimental Section

Materials. 2-Butanone (≥ 0.995) and *N*-methylaniline (≥ 0.98) were from Fluka, and aniline (≥ 0.995) and pyridine (≥ 0.995) were from Riedel de Haën and used without further purification (purities expressed in mass fraction). The ρ and u values of the pure liquids are in good agreement with those from the literature (Table 1).

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.[5]

The densities and speeds of sound of both pure liquids and of the mixtures were measured using a vibrating-tube densimeter and a sound analyzer (Anton Paar model DSA-5000) automatically thermostatted within ± 0.01 K. The calibration of the apparatus was carried out with deionized double-distilled water, heptane, octane, isooctane, cyclohexane, and benzene, using ρ values from the literature.[6−8] The accuracy for the ρ and u measurements is ± $1 \cdot 10^{-2}$ kg·m^{-3} and ± 0.1 m·s^{-1}, respectively, and the corresponding precisions are ± $1 \cdot 10^{-3}$ kg·m^{-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.[9−12] The accuracy in V^E is believed to be less than ± $(0.01|V_{max}^E| + 0.005)$ $cm^3 \cdot mol^{-1}$, where $|V_{max}^E|$ denotes the maximum experimental value of the excess molar

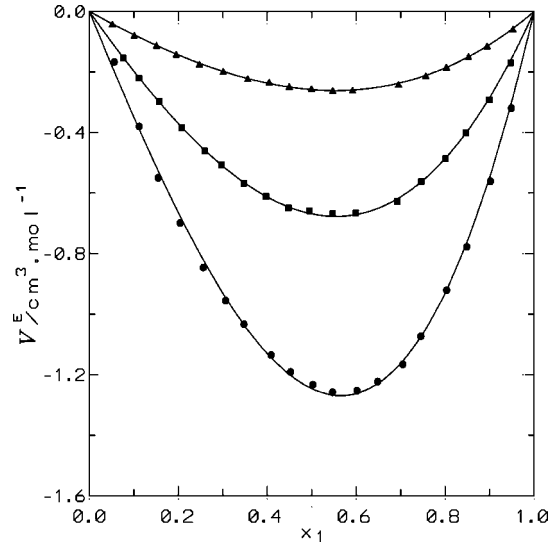

Figure 1. Excess molar volumes for the 2-butanone (1) + aromatic amine (2) systems at atmospheric pressure and 298.15 K. Full symbols, experimental values (this work): ●, aniline; ■, *N*-methylaniline; ▲, pyridine. Solid lines, calculations with eq 7 using the coefficients from Table 4.

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Table 1. Physical Properties of Pure Compounds, 2-Butanone, Aniline, *N*-Methylaniline, and Pyridine at Temperature *T*[a]

		2-butanone		aniline		*N*-methylaniline		pyridine	
property	*T*/K	this work	lit.	this work	lit.	this work	lit.	this work	lit.
ρ/g·cm^{-3}	293.15	0.805080	0.8049[b]	1.021844	1.02104[c]	0.986295		0.983163	0.98319[b]
			0.80495[d]						
	298.15	0.799861	0.79974[d]	1.017511	1.01710[c]	0.982278	0.98206[e]	0.978138	0.97824[b]
			0.79992[f]		1.01744[e]				0.97810[g]
			0.7997[h]		1.01741[i]				0.97782[j]
	303.15	0.794636	0.79448[d]	1.013232	1.01306[b]	0.978284	0.9782[k]	0.973148	0.97286[l]
			0.79464[f]		1.0128[k]				0.9731[m]
u/m·s^{-1}	293.15	1212.0	1213[d]	1657.01	1651.3[n]	1582.5		1436.6	
	298.15	1190.8	1192[d]	1637.8	1634[i]	1563.9		1416.2	1416.1[j]
			1195[o]		1615.2[k]				1412.3[p]
					1632.8[n]				
	303.15	1170.6	1171[d]	1619.3	1614.5[n]	1546.0	1548.2[k]	1396.9	1398[j]
									1395.4[m]
α_P/10^{-3}K^{-1}	298.15	1.31	1.31[d]	0.846	0.850[b]	0.816	0.813[b]	1.024	1.07[b,j]
κ_S/TPa^{-1}	293.15	845.5	844[d]	356.42		404.9		492.8	
	298.15	881.7	880[d]	366.4	368[b]	416.2		509.7	509.92[j]
			875.8[o]						
	303.15	918.3	918[d]	376.4	379[k]	427.7	427[k]	526.6	525[j]
									528.8[m]
κ_T/TPa^{-1}	298.15	1169.6	1188[b]	467.1	472[c]	520.7		701.9	
C_P/J·mol^{-1}·K^{-1}	298.15		159.2[q]		194.1[r]		207.1[r]		131.5[s]

[a] ρ, density; u, speed of sound; α_P, isobaric thermal expansion coefficient; κ_S, adiabatic compressibility; κ_T, isothermal compressibility [calculated from $\kappa_T = \kappa_S + ((TV\alpha_P^2)/C_P)$]; and C_P, isobaric heat capacity. [b] Ref 6. [c] Ref 22. [d] Ref 23. [e] Ref 24. [f] Ref 25. [g] Ref 26. [h] Ref 27. [i] Ref 28. [j] Ref 29. [k] Ref 30. [l] Ref 31. [m] Ref 32. [n] Ref 33. [o] Ref 34. [p] Ref 35. [q] Ref 36. [r] Ref 37. [s] Ref 38.

volume with respect to the mole fraction. The accuracy of the deviations of u from the ideal behavior is estimated to be 0.3 m·s^{-1}.

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 equation

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

For an ideal mixture at the same temperature and pressure as the system under study, the values F^{id} of the thermodynamic property, F, are calculated using the equations[9,13]

$$F^{id} = x_1F_1 + x_2F_2 \qquad (F = V, C_P) \tag{2}$$

and

$$F^{id} = \phi_1F_1 + \phi_2F_2 \qquad (F = \alpha_P;\kappa_T) \tag{3}$$

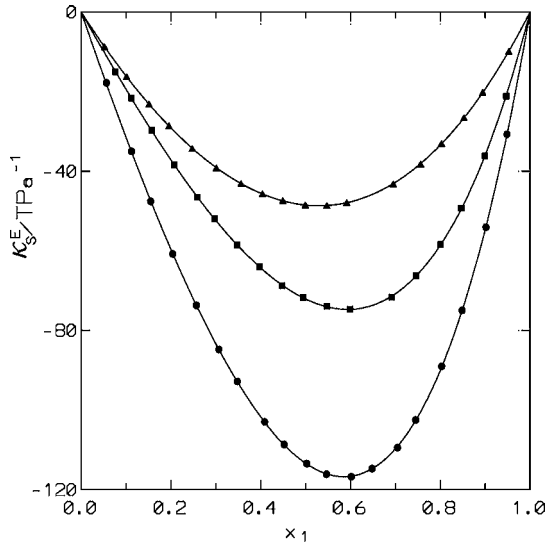

Figure 2. κ_S^E for the 2-butanone (1) + aromatic amine (2) systems at atmospheric pressure and 298.15 K. Symbols, experimental data (this work): ●, aniline; ■, *N*-methylaniline; ▲, pyridine. Solid lines, calculations with eq 7 using the coefficients from Table 4.

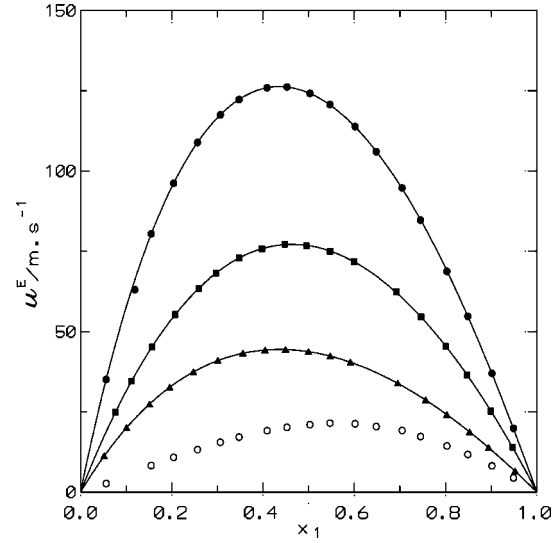

Figure 3. u^E for the 2-butanone (1) + aromatic amine (2) systems at atmospheric pressure and 298.15 K. Full symbols, experimental data (this work): ●, aniline; ■, *N*-methylaniline; ▲, pyridine. Open symbols, $\Delta u = u - (x_1u_1 + x_2u_2)$ for the aniline mixture. Solid lines, calculations with eq 7 using the coefficients from Table 4.

Table 2. Densities, ρ, Molar Excess Volumes, V^E, and Speed of Sound for 2-Butanone (1) + Aromatic Amine (2) Mixtures at Temperature T

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}
2-Butanone (1) + Aniline (2); T/K = 293.15							
0.0580	1.011292	−0.1639	1633.73	0.5443	0.917103	−1.213	1435.84
0.1122	1.001344	−0.3132	1612.22	0.6120	0.902143	−1.206	1405.44
0.1576	0.993678	−0.5028	1594.71	0.6480	0.894022	−1.189	1388.95
0.2052	0.985068	−0.6538	1576.01	0.7044	0.880787	−1.109	1362.11
0.2543	0.976056	−0.8029	1556.68	0.7754	0.863737	−0.9697	1328.59
0.3043	0.966420	−0.9143	1536.62	0.8081	0.855598	−0.8772	1311.28
0.3562	0.956208	−1.016	1515.48	0.8493	0.845213	−0.7431	1290.46
0.4059	0.946279	−1.102	1495.18	0.9027	0.831249	−0.5139	1262.94
0.4530	0.936500	−1.152	1475.25	0.9476	0.819373	−0.3025	1239.59
0.5048	0.925617	−1.196	1453.16				
2-Butanone (1) + Aniline (2); T/K = 298.15							
0.0560	1.007337	−0.1670	1615.43	0.5467	0.911916	−1.258	1414.88
0.1188	0.997647	−0.3801	1593.59	0.6019	0.899666	−1.253	1390.03
0.1547	0.990216	−0.5500	1576.89	0.6481	0.889131	−1.223	1368.49
0.2038	0.981189	−0.6992	1557.51	0.7048	0.875989	−1.116	1341.93
0.2563	0.971230	−0.8367	1536.46	0.7451	0.866153	−1.073	1322.03
0.3064	0.961559	−0.9548	1516.35	0.8030	0.851853	−0.9208	1293.23
0.3474	0.953414	−1.033	1499.63	0.8487	0.840349	−0.7778	1270.14
0.4089	0.940989	−1.135	1474.12	0.9019	0.826554	−0.5614	1242.80
0.4523	0.932032	−1.191	1455.79	0.9489	0.813934	−0.3197	1218.03
0.5026	0.921385	−1.233	1434.14				
2-Butanone (1) + Aniline (2); T/K = 303.15							
0.0582	1.002610	−0.1799	1596.11	0.5537	0.905656	−1.297	1392.66
0.1097	0.993104	−0.3320	1575.62	0.6044	0.894417	−1.300	1369.77
0.1485	0.986049	−0.4610	1560.26	0.6434	0.885415	−1.265	1351.53
0.2050	0.975667	−0.6424	1537.97	0.7038	0.871181	−1.186	1322.64
0.2507	0.967388	−0.8030	1520.34	0.7716	0.854721	−1.043	1289.42
0.3064	0.956964	−0.9736	1497.88	0.8079	0.845614	−0.9332	1271.08
0.3426	0.949873	−1.058	1482.95	0.8481	0.835388	−0.7966	1250.64
0.4140	0.935434	−1.183	1453.33	0.8988	0.822096	−0.5788	1224.22
0.4470	0.928634	−1.231	1439.45	0.9466	0.809221	−0.3274	1199.01
0.4910	0.919218	−1.262	1420.26				
2-Butanone (1) + *N*-Methylaniline (2); T/K = 293.15							
0.0627	0.977942	−0.1220	1562.93	0.4907	0.912022	−0.6464	1418.46
0.1133	0.970977	−0.2140	1546.90	0.5508	0.901210	−0.6519	1396.18
0.1564	0.964888	−0.2859	1532.86	0.5959	0.892779	−0.6421	1378.86
0.2058	0.957750	−0.3659	1516.97	0.6529	0.881753	−0.6126	1356.64
0.2538	0.950572	−0.4313	1501.02	0.7489	0.862241	−0.5203	1318.20
0.3018	0.943182	−0.4888	1484.81	0.7938	0.852894	−0.4688	1300.01
0.3464	0.936057	−0.5388	1469.41	0.8492	0.840630	−0.3749	1276.95
0.3938	0.928444	−0.5814	1453.01	0.8981	0.829680	−0.2925	1256.68
0.4435	0.920205	−0.6256	1435.57	0.9525	0.816716	−0.1415	1232.87
2-Butanone (1) + *N*-Methylaniline (2); T/K = 298.15							
0.0760	0.972066	−0.1540	1540.12	0.4950	0.906694	−0.6593	1397.25
0.1115	0.967149	−0.2205	1528.78	0.5471	0.897284	−0.6678	1377.77
0.1566	0.960718	−0.2977	1514.16	0.5992	0.887579	−0.6667	1357.93
0.2076	0.953334	−0.3850	1497.60	0.6921	0.869471	−0.6281	1321.67
0.2589	0.945633	−0.4612	1480.59	0.7463	0.858202	−0.5624	1299.55
0.2967	0.939765	−0.5070	1467.74	0.8007	0.846555	−0.4866	1276.99
0.3471	0.931809	−0.5683	1450.49	0.8470	0.836277	−0.4009	1257.46
0.3973	0.923563	−0.6117	1432.77	0.8993	0.824346	−0.2918	1235.12
0.4477	0.915055	−0.6495	1414.78	0.9472	0.813000	−0.1697	1214.45
2-Butanone (1) + *N*-Methylaniline (2); T/K = 303.15							
0.0641	0.969669	−0.1386	1525.99	0.5536	0.891605	−0.7015	1356.87
0.1123	0.962964	−0.2330	1510.65	0.5984	0.883203	−0.6998	1339.70
0.1581	0.956434	−0.3172	1495.93	0.6489	0.873485	−0.6921	1320.14
0.2036	0.949789	−0.3983	1481.08	0.6969	0.863705	−0.6432	1300.71
0.2591	0.941381	−0.4795	1462.50	0.7543	0.851719	−0.5773	1277.07
0.3061	0.934049	−0.5407	1446.49	0.8047	0.840797	−0.4991	1256.00
0.3513	0.926789	−0.5935	1430.76	0.8497	0.830818	−0.4237	1237.07
0.4022	0.918424	−0.6449	1412.90	0.8965	0.819999	−0.3135	1216.77
0.4472	0.910653	−0.6670	1396.45	0.9524	0.806615	−0.1599	1192.15
0.5025	0.900926	−0.6939	1376.10				
2-Butanone (1) + Pyridine (2); T/K = 293.15							
0.0584	0.972180	−0.0437	1424.61	0.5481	0.883417	−0.2490	1318.24
0.1010	0.964232	−0.0739	1415.75	0.6003	0.874227	−0.2456	1306.41
0.1557	0.954114	−0.1098	1404.26	0.6425	0.866814	−0.2380	1296.69
0.2073	0.944625	−0.1412	1393.33	0.6948	0.857663	−0.2235	1284.55
0.2479	0.937177	−0.1609	1384.58	0.7267	0.852119	−0.2131	1277.11
0.2928	0.929036	−0.1852	1374.92	0.7519	0.847742	−0.2017	1271.21

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}
0.3534	0.918142	−0.2136	1361.81	0.8053	0.838532	−0.1764	1258.66
0.3992	0.909880	−0.2257	1351.64	0.8550	0.829934	−0.1409	1246.86
0.4535	0.900169	−0.2381	1339.54	0.8907	0.823832	−0.1165	1238.36
0.4962	0.892606	−0.2460	1330.03	0.9459	0.814255	−0.0531	1224.94
0.5461	0.883748	−0.2465	1318.73				
			2-Butanone (1) + Pyridine (2); T/K = 298.15				
0.0517	0.968413	−0.0418	1405.65	0.4994	0.886914	−0.2558	1308.40
0.1009	0.959234	−0.0786	1395.36	0.5472	0.878480	−0.2611	1297.57
0.1510	0.949923	−0.1117	1384.77	0.5916	0.870664	−0.2603	1287.41
0.1952	0.941811	−0.1419	1375.38	0.6951	0.852550	−0.2410	1263.53
0.2473	0.932304	−0.1740	1364.24	0.7563	0.841861	−0.2122	1249.19
0.3010	0.922495	−0.1985	1352.53	0.8029	0.833777	−0.1842	1238.08
0.3559	0.912585	−0.2225	1340.44	0.8525	0.825199	−0.1488	1226.24
0.4041	0.903885	−0.2342	1329.73	0.8944	0.817974	−0.1139	1216.21
0.4494	0.895816	−0.2479	1319.62	0.9525	0.808018	−0.0581	1202.26
			2-Butanone (1) + Pyridine (2); T/K = 303.15				
0.0589	0.962089	−0.0516	1384.67	0.5482	0.873285	−0.2784	1277.68
0.1170	0.951238	−0.0947	1372.47	0.5967	0.864734	−0.2769	1266.56
0.1620	0.942929	−0.1279	1362.93	0.6484	0.855625	−0.2668	1254.57
0.2056	0.934925	−0.1587	1353.60	0.6972	0.847054	−0.2492	1243.11
0.2489	0.926990	−0.1849	1344.25	0.7446	0.838804	−0.2303	1232.07
0.3075	0.916353	−0.2169	1331.49	0.7952	0.829990	−0.2008	1220.01
0.3506	0.908572	−0.2363	1322.05	0.8476	0.820935	−0.1654	1207.59
0.4016	0.899409	−0.2567	1310.80	0.8928	0.813143	−0.1269	1196.75
0.4494	0.890804	−0.2643	1299.97	0.9371	0.805515	−0.0821	1186.04
0.4959	0.882520	−0.2718	1289.48				

where C_P is the isobaric heat capacity; $\phi_i = [(x_i V_i)/V^{id}]$ is the volume fraction; κ_T is 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[13]

$$\kappa_S^{id} = \kappa_T^{id} - \frac{TV^{id}(\alpha_P^{id})^2}{C_P^{id}} \tag{4}$$

and

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

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

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

Results and Discussion

Table 2 lists values of densities, calculated V^E, and u vs x_1, the mole fraction of the 2-butanone. Table 3 contains the derived quantities κ_S^E, u^E, and α_P^E. The data were fitted by unweighted least-squares polynomial regression to the equation

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

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[14] 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

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

where N is the number of direct experimental values. Results on V^E, κ_S^E, and u^E are shown graphically in Figures 1 to 3. 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.

It is known that V^E is the result of several opposing effects. Interactions between like molecules lead to increased V^E values, while negative contributions to V^E arise from interactions between unlike molecules, or structural effects as changes in free volume, or interstitial accommodation. For the investigated systems, the negative V^E values determined here may be due to interactions between unlike molecules. In fact, the large negative H^E of the 2-propanone + aniline mixture[15] (−1224 J·mol^{-1}) reveals strong acetone−aniline interactions. In addition, the strength of such interactions has been previously estimated to be[3] −30.5 kJ·mol^{-1}. The common value used for the enthalpy of H-bonds between 1-alkanol molecules in the ERAS model is[16,17] −25.1 kJ·mol^{-1}. This means that the propanone−aniline interactions are stronger. Mixtures such as amine + 1-alcohol, or + $CHCl_3$, characterized also by strong interactions between unlike molecules,[17,18] show V^E values similar to those listed in Table 2. For example, V^E(1-propanol + propylamine)[19] = −1.315 cm^3·mol^{-1} and V^E(trichloromethane + butylamine)[20] = −0.368 cm^3·mol^{-1}. The negative $(\partial V^E/\partial T)_P$ and κ_S^E values and the positive u^E values are in agreement with the existence of strong ketone−amine interactions in the investigated systems. The former have been interpreted in terms of a decrease in the molar volume of complex formation, which overcompensates for the decrease in the extent of complex formation, and have been encountered, e.g., in amine + trichloromethane mixtures.[20,21]

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) + Aromatic Amine (2) Mixtures

x_1	κ_S^E / TPa^{-1}	u^E / $m \cdot s^{-1}$	α_P^E / $10^{-6} \cdot K^{-1}$
	2-Butanone (1) + Aniline (2)		
0.0560	−17.81	35.09	31.31
0.1118	−34.99	63.07	30.26
0.1547	−47.57	80.43	16.73
0.2038	−60.78	96.14	−4.79
0.2563	−73.72	108.86	−29.43
0.3064	−84.78	117.47	−50.41
0.3474	−92.82	122.26	−63.97
0.4089	−102.98	125.89	−76.98
0.4523	−108.67	126.14	−80.88
0.5026	−113.48	124.17	−80.65
0.5467	−116.13	120.69	−77.40
0.6019	−116.76	113.83	−70.85
0.6481	−114.72	105.99	−64.76
0.7048	−109.46	94.68	−58.27
0.7451	−102.50	84.64	−54.39
0.8030	−89.03	68.71	−50.42
0.8487	−74.99	54.78	−47.37
0.9019	−54.06	37.03	−40.65
0.9489	−30.72	19.85	−27.78
	2-Butanone (1) + *N*-Methylaniline (2)		
0.0760	−15.02	24.91	−13.58
0.1115	−21.65	34.55	−18.59
0.1566	−29.73	45.20	−24.02
0.2076	−38.43	55.34	−29.22
0.2589	−46.52	63.47	−33.65
0.2967	−51.91	68.10	−36.52
0.3471	−58.54	72.86	−40.06
0.3973	−64.06	75.72	−43.22
0.4477	−68.76	77.14	−46.20
0.4950	−71.76	76.72	−48.59
0.5471	−73.96	74.94	−50.96
0.5992	−74.70	71.71	−52.80
0.6921	−71.66	62.41	−53.79
0.7463	−66.31	54.58	−52.02
0.8007	−58.42	45.38	−48.04
0.8470	−49.25	36.42	−42.21
0.8993	−36.11	25.20	−32.38
0.9472	−21.13	13.98	−19.51
	2-Butanone (1) + Pyridine (2)		
0.0517	−8.76	11.28	−5.54
0.1009	−16.26	20.05	−10.38
0.1510	−23.14	27.37	−14.87
0.1952	−28.62	32.62	−18.48
0.2473	−34.30	37.48	−22.24
0.3010	−39.15	41.02	−25.48
0.3559	−43.09	43.27	−28.17
0.4041	−45.66	44.23	−29.90
0.4494	−47.41	44.39	−31.11
0.4994	−48.48	43.76	−31.81
0.5472	−48.62	42.37	−31.92
0.5916	−47.91	40.45	−31.45
0.6951	−43.22	33.91	−28.26
0.7563	−38.20	28.73	−24.86
0.8029	−33.07	24.09	−21.53
0.8525	−26.58	18.72	−17.27
0.8944	−20.20	13.83	−13.07
0.9525	−9.92	6.52	−6.37

Both magnitudes V^E and κ_S^E increase in the sequence: aniline < *N*-methylaniline < pyridine (Figures 1 and 2), while u^E decreases in the opposite way (Figure 3). This may be interpreted assuming that the new 2-butanone−amine interactions created upon mixing are more easily formed in the case of aniline solutions due to the larger ability of aniline to form H-bonds with the oxygen atom of the ketone, related with the presence of the NH_2 group in this amine.

Table 4. Coefficients A_i and Standard Deviations, $\sigma(F^E)$ (Equation 8), for Representation of the F^E [a] Property at Temperature *T* for 2-Butanone (1) + Aromatic Amine (2) Systems by Equation 7

system	*T*/K	property F^E	A_0	A_1	A_2	A_3	$\sigma(F^E)$
2-butanone + aniline	293.15	V^E	−4.79	−1.40			0.018
	298.15	V^E	−4.985	−1.38			0.016
		u^E	497.3	−120.3	49.5	−31	0.12
		κ_S^E	−453.5	−155.1	−40.64	−9	0.16
		α_P^E	−322.94	85.2	430.5	−927.8	0.09
	303.15	V^E	−5.135	−1.35	0.39	−0.85	0.009
2-butanone + *N*-methylaniline	293.15	V^E	−2.561	−0.55			0.007
	298.15	V^E	−2.677	−0.604			0.005
		u^E	306.83	−43.9	12.0		0.11
		κ_S^E	−288.5	−108.0	−30.5	−10	0.13
		α_P^E	−195.56	−98.1	−122.0	−11.5	0.05
	303.15	V^E	−2.782	−0.645	−0.11		0.004
2-butanone + pyridine	293.15	V^E	−0.982	−0.209			0.002
	298.15	V^E	−1.032	−0.225			0.002
		u^E	174.97	−43.3	13.8	−5.8	0.04
		κ_S^E	−194.03	−22.3	−4.7		0.06
		α_P^E	−127.34	−15.26	1.18		0.02
	303.15	V^E	−1.102	−0.232			0.002

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

The composition dependence of the V^E and κ_S^E curves is similar and is the same for the studied mixtures (Figures 1 and 2). These curves are shifted toward higher mole fractions of 2-butanone and show a minimum near $x_1 = 0.6$. Figure 3 compares, for the aniline system, u^E and $\Delta u = u - (x_1u_1 + x_2u_2)$. The large difference between these quantities remarks the necessity of defining correctly the ideal values.[13]

Finally, it should be mentioned that the values of the excess functions determined in this work are similar to those obtained for the 2-propanone mixtures.[3] That is, interactions between unlike molecules are similar in solutions including 2-butanone or acetone.

Conclusions

In this work, we have determined V^E, u^E, α_P^E, and κ_S^E for mixtures including 2-butanone and aromatic amines. The V^E and κ_S^E magnitudes are negative and increase in the sequence: aniline < *N*-methylaniline < pyridine. In contrast, u^E is positive and changes in the opposite way. The data have been interpreted in terms of rather strong 2-butanone−amine interactions.

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