

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

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Densities, ρ , and speeds of sound, u , of 2-propanone + 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 , at 298.15 K. V^E and κ_S^E are both negative magnitudes and increase in the same sequence: aniline < *N*-methylaniline < pyridine. The V^E and κ_S^E curves are shifted toward higher mole fractions of 2-propanone. The data have been interpreted assuming strong acetone–amine interactions and weak structural effects.

Introduction

Amides, amino acids, peptides, and their derivatives are of interest because they are simple models in biochemistry. *N*-Methylformamide possesses the basic (–CO) and acidic (–NH) groups of the very common, in nature, peptide bond.¹ As a matter of fact, proteins are polymers of amino acids linked to each other by peptide bonds. Cyclic amides are also of importance because they are related to structural problems in biochemistry. 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 So, the aqueous solution of dimethylformamide is a model solvent representing the environment of the interior of proteins. Amides have many practical applications. For example, 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 then pertinent to gain insight into amide solutions. In this first article, 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-propanone + aniline, + *N*-methylaniline, or + pyridine mixtures.

Experimental Section

Material. 2-Propanone (67-64-1) and *N*-methylaniline (100-61-8) were from Fluka, and aniline (62-53-3) and pyridine (110-86-1) were from Riedel de Haën and used without further purification. Their purity, expressed in mass fraction, was ≥ 0.995 , ≥ 0.98 , ≥ 0.995 , and ≥ 0.995 , respectively. The ρ and u values of the pure liquids are in good agreement with those from the literature (Table 1).

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Apparatus and Procedure. Binary mixtures were prepared by mass in small vessels of about 10 cm³. 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.⁴

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.^{5–7} The accuracy for the ρ and u measurements is $\pm 1 \cdot 10^{-2}$ kg·m⁻³ and ± 0.1 m·s⁻¹, respectively, and the corresponding precisions are $\pm 1 \cdot 10^{-3}$ 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.^{8–11} The accuracy in V^E is believed to be less than $\pm (0.01|V_{\max}^E| + 0.005)\text{cm}^3 \cdot \text{mol}^{-1}$, where $|V_{\max}^E|$ 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 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

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

property	T/K	2-propanone		aniline		<i>N</i> -methylaniline		pyridine	
		this work	lit.	this work	lit.	this work	lit.	this work	lit.
$\rho/g \cdot cm^{-3}$	293.15	0.790694	0.78998 ^b	1.021702	1.02104 ^c	0.986077		0.983053	0.98319 ^b
	298.15	0.785320	0.784431 ^d	1.017406	1.01710 ^c	0.982066	0.98206 ^e	0.978050	0.97824 ^b
			0.78428 ^f		1.01744 ^e				0.97810 ^g
$u/m \cdot s^{-1}$	303.15	0.778812	0.77914 ^f	1.013045	1.01284 ^c	0.978011		0.972980	0.97286 ^j
	293.15	1182.8	1192 ^k	1657.0	1651.3 ^l	1582.3		1436.7	
	298.15	1160.7	1161.72 ^d	1638.6	1634 ⁱ	1564.4		1416.7	
			1154 ^f		1632.8 ^l				
			1160.6 ^h						
$\alpha_p/10^{-3} K^{-1}$	303.15	1138.7	1132.2 ^f	1619.2	1614.5 ^l	1545.5		1396.6	1398 ^j
	298.15	1.56	1.426 ^f	0.85	0.850 ^b	0.82		1.03	1.07 ^b
κ_S/TPa^{-1}	293.15	903.9		356.5		405.0		492.8	
	298.15	945.1	944.59 ^d	366.1	368 ^b	416.1		509.5	
κ_T/TPa^{-1}	303.15	990.4	1003 ^f	376.5		428.1		526.9	525 ^j
	298.15	1373.6	1324 ^b	467.9	472 ^c	522.1		704	
			1330 ^f						
$C_p/J \cdot mol^{-1} \cdot K^{-1}$	298.15		124.9 ^b		194.1 ^m		207.1 ^m		131.5 ⁿ

^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 5. ^c Ref 33. ^d Ref 21. ^e Ref 34. ^f Ref 35. ^g Ref 36. ^h Ref 37. ⁱ Ref 38. ^j Ref 39. ^k Ref 40. ^l Ref 41. ^m Ref 42. ⁿ Ref 20.

$$\kappa_S = \frac{1}{\rho u^2} \quad (1)$$

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^{8,12}

$$F^{id} = x_1 F_1 + x_2 F_2 \quad (F = V, C_p) \quad (2)$$

and

$$F^{id} = \phi_1 F_1 + \phi_2 F_2 \quad (F = \alpha_p; \kappa_T) \quad (3)$$

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 is

the F value of component i , respectively. For κ_S and u , the ideal values are calculated according to¹²

$$\kappa_S^{id} = \kappa_T^{id} - \frac{TV^{id}\alpha_p^{id2}}{C_p^{id}} \quad (4)$$

and

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

where $\rho^{id} = (x_1 M_1 + x_2 M_2)/V^{id}$ (M_i , molecular mass of the i component). In this work, we have determined the excess functions

$$F^E = F - F^{id} \quad (6)$$

Results and Discussion

Table 2 lists values of densities, calculated V^E , and u vs x_1 , the mole fraction of 2-propanone. Table 3 contains the derived

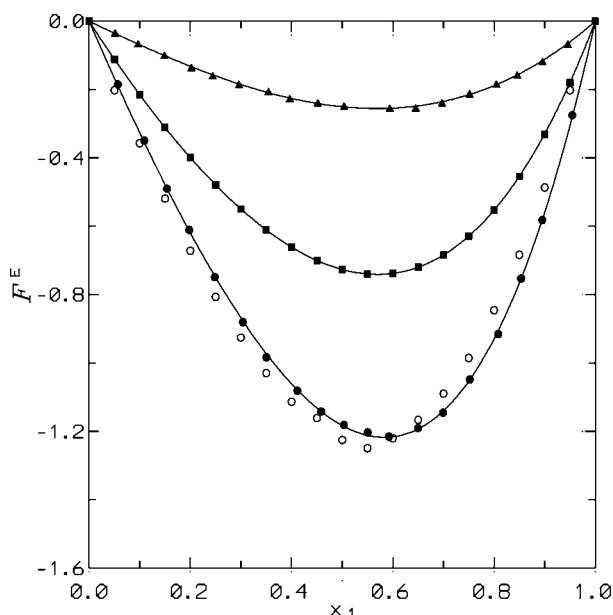


Figure 1. Excess molar functions for the 2-propanone (1) + aromatic amine (2) systems at atmospheric pressure and 298.15 K. Full symbols, $V^E/cm^3 \cdot mol^{-1}$ (this work): ●, aniline; ■, *N*-methylaniline; ▲, pyridine. Open symbols, $(H^E/J \cdot mol^{-1})/100$ for the aniline solution.²¹ Solid lines, calculations with eq 7 using the coefficients from Table 4.

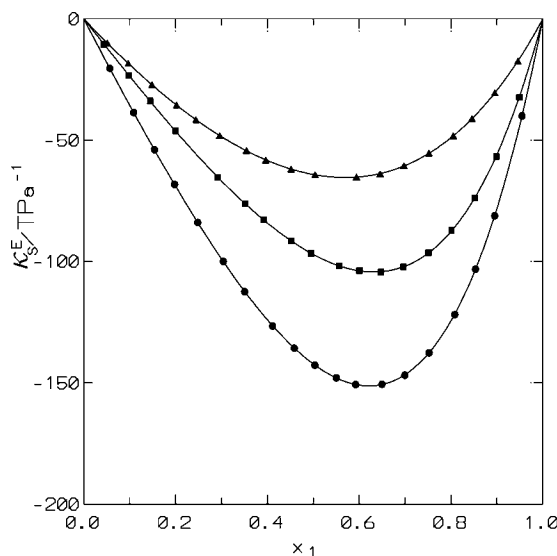


Figure 2. κ_S^E for the 2-propanone (1) + aromatic amine (2) systems at atmospheric pressure and 298.15 K. Symbols, experimental data (this work): ●, aniline; ■, *N*-methylaniline; ▲, pyridine. Solid lines, calculations with eq 7 using the coefficients from Table 4.

Table 2. Densities, ρ , Molar Excess Volumes, V^E , and Deviations from the Ideal Behavior of the Speed of Sound for 2-Propanone (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-Propanone (1) + Aniline (2); $T/K = 293.15$							
0.0522	1.013709	-0.1611	1638.35	0.5497	0.920272	-1.160	1437.53
0.1078	1.004965	-0.3316	1618.48	0.5830	0.912529	-1.169	1421.64
0.1567	0.996941	-0.4681	1600.65	0.6446	0.897535	-1.153	1390.65
0.2074	0.988429	-0.6142	1581.82	0.6911	0.885684	-1.118	1366.49
0.2490	0.981269	-0.7314	1566.20	0.7465	0.870629	-1.024	1335.85
0.3016	0.971707	-0.8513	1545.76	0.8046	0.854022	-0.8819	1302.73
0.3454	0.963326	-0.9303	1527.88	0.8497	0.840545	-0.7433	1276.21
0.3832	0.955799	-0.9842	1512.13	0.9045	0.823238	-0.5220	1242.96
0.4313	0.946013	-1.052	1491.44	0.9475	0.809118	-0.3046	1216.10
0.4908	0.933416	-1.120	1465.03				
2-Propanone (1) + Aniline (2); $T/K = 298.15$							
0.0569	1.008670	-0.1850	1618.3	0.5501	0.915531	-1.203	1417.8
0.1088	1.000436	-0.3486	1599.6	0.5922	0.905703	-1.215	1397.3
0.1539	0.993118	-0.4898	1583.2	0.6499	0.891425	-1.190	1367.7
0.1978	0.985694	-0.6111	1566.7	0.6993	0.878643	-1.145	1341.6
0.2484	0.976895	-0.7492	1547.4	0.7522	0.864125	-1.048	1312.1
0.3039	0.966770	-0.8805	1525.8	0.8082	0.848052	-0.9146	1279.9
0.3505	0.957976	-0.9826	1507.0	0.8533	0.834272	-0.7530	1252.8
0.4114	0.945773	-1.081	1481.1	0.8951	0.821048	-0.5816	1227.3
0.4585	0.935933	-1.142	1460.4	0.9545	0.801258	-0.2750	1190.0
0.5035	0.926122	-1.181	1439.9				
2-Propanone (1) + Aniline (2); $T/K = 303.15$							
0.0515	1.005017	-0.1691	1600.76	0.5502	0.910191	-1.261	1397.55
0.1002	0.997272	-0.3311	1583.36	0.6037	0.897422	-1.269	1371.13
0.1475	0.989506	-0.4805	1566.03	0.6464	0.886697	-1.246	1348.94
0.1926	0.981799	-0.6104	1549.06	0.6975	0.873362	-1.197	1321.68
0.2399	0.973527	-0.7470	1531.02	0.7548	0.857721	-1.111	1290.18
0.3024	0.962003	-0.8977	1506.37	0.8078	0.842147	-0.9626	1259.19
0.3475	0.953088	-0.9716	1487.41	0.8567	0.827148	-0.7897	1229.86
0.3947	0.943989	-1.087	1468.09	0.9014	0.812779	-0.5938	1202.26
0.4503	0.932550	-1.183	1444.06	0.9494	0.796575	-0.3342	1171.73
0.4979	0.922075	-1.225	1422.10				
2-Propanone (1) + <i>N</i> -Methylaniline (2); $T/K = 293.15$							
0.0565	0.979562	-0.1177	1566.00	0.5489	0.905091	-0.6971	1396.72
0.1032	0.973934	-0.2094	1552.20	0.5965	0.895722	-0.6994	1377.18
0.1494	0.968145	-0.2955	1538.20	0.6485	0.884852	-0.6849	1354.94
0.1916	0.962605	-0.3664	1524.93	0.7018	0.873046	-0.6508	1331.41
0.2510	0.954413	-0.4576	1505.74	0.7472	0.862270	-0.5948	1310.35
0.2952	0.948053	-0.5209	1491.11	0.8020	0.848690	-0.5245	1284.63
0.3555	0.938912	-0.5953	1470.34	0.8563	0.834277	-0.4247	1258.05
0.4039	0.931040	-0.6344	1452.78	0.9053	0.820343	-0.3047	1233.13
0.4478	0.923576	-0.6619	1436.33	0.9548	0.805391	-0.1564	1207.00
0.4981	0.914659	-0.6888	1417.03				
2-Propanone (1) + <i>N</i> -Methylaniline (2); $T/K = 298.15$							
0.0440	0.977005	-0.0971	1551.80	0.5563	0.899086	-0.7343	1374.44
0.0984	0.970455	-0.2105	1535.67	0.6004	0.890231	-0.7371	1355.78
0.1447	0.964607	-0.2985	1521.51	0.6473	0.880387	-0.7266	1335.71
0.1996	0.957353	-0.3971	1504.22	0.6962	0.869434	-0.6904	1313.74
0.2503	0.950290	-0.4773	1487.65	0.7506	0.856501	-0.6268	1288.41
0.2919	0.944327	-0.5456	1474.09	0.8009	0.843758	-0.5449	1264.11
0.3511	0.935283	-0.6199	1453.29	0.8518	0.830205	-0.4516	1238.96
0.3924	0.928532	-0.6516	1438.13	0.8986	0.816915	-0.3377	1215.04
0.4520	0.918415	-0.6986	1415.84	0.9488	0.801799	-0.1884	1188.58
0.4948	0.910794	-0.7256	1399.32				
2-Propanone (1) + <i>N</i> -Methylaniline (2); $T/K = 303.15$							
0.0461	0.972638	-0.1079	1532.14	0.5507	0.895228	-0.7946	1357.06
0.0934	0.966889	-0.2135	1518.12	0.5949	0.886274	-0.7909	1338.42
0.1524	0.959343	-0.3337	1500.03	0.6467	0.875210	-0.7715	1315.78
0.1937	0.953815	-0.4108	1486.97	0.6928	0.864807	-0.7384	1295.01
0.2442	0.946596	-0.4829	1470.07	0.7424	0.852961	-0.6836	1271.81
0.2834	0.941069	-0.5653	1457.52	0.7993	0.838524	-0.5956	1244.29
0.3357	0.933026	-0.6316	1439.18	0.8469	0.825646	-0.4966	1220.47
0.3991	0.922737	-0.7029	1416.25	0.8977	0.811117	-0.3691	1194.30
0.4460	0.914773	-0.7526	1399.25	0.9484	0.795598	-0.2065	1167.27
0.4904	0.906677	-0.7704	1381.24				

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
2-Propanone (1) + Pyridine (2); $T/K = 293.15$							
0.0577	0.973393	-0.0418	1424.88	0.5519	0.884082	-0.2351	1309.32
0.1007	0.966028	-0.0648	1415.57	0.5969	0.875296	-0.2332	1297.67
0.1536	0.956946	-0.0993	1404.09	0.6425	0.866297	-0.2290	1285.63
0.2043	0.948163	-0.1319	1392.96	0.7030	0.854168	-0.2181	1269.32
0.2219	0.945011	-0.1369	1389.00	0.7504	0.844514	-0.2028	1256.33
0.2968	0.931713	-0.1766	1371.80	0.8066	0.832904	-0.1802	1240.56
0.3537	0.921354	-0.1952	1358.39	0.8569	0.822218	-0.1428	1225.97
0.4051	0.911899	-0.2117	1346.07	0.9019	0.812518	-0.1041	1212.66
0.5191	0.890383	-0.2319	1317.70	0.9456	0.803006	-0.0652	1199.55
2-Propanone (1) + Pyridine (2); $T/K = 298.15$							
0.0514	0.969365	-0.0338	1405.83	0.5448	0.880262	-0.2568	1290.28
0.0969	0.961623	-0.0661	1396.12	0.5940	0.870649	-0.2570	1277.31
0.1486	0.952705	-0.0997	1384.77	0.6454	0.860492	-0.2535	1263.72
0.2023	0.943375	-0.1356	1372.83	0.6971	0.850006	-0.2349	1249.50
0.2444	0.935930	-0.1598	1363.28	0.7518	0.838783	-0.2125	1234.34
0.2960	0.926692	-0.1850	1351.30	0.8049	0.827707	-0.1844	1219.28
0.3544	0.916021	-0.2062	1337.42	0.8456	0.819096	-0.1575	1207.46
0.3965	0.908330	-0.2268	1327.36	0.8955	0.808385	-0.1177	1192.71
0.4516	0.898006	-0.2393	1313.79	0.9456	0.797415	-0.0666	1177.52
0.5036	0.888125	-0.2488	1300.66				
2-Propanone (1) + Pyridine (2); $T/K = 303.15$							
0.0493	0.964637	-0.0401	1386.22	0.4970	0.883593	-0.2683	1281.42
0.0954	0.956714	-0.0743	1376.21	0.5412	0.875069	-0.2759	1270.11
0.1463	0.947874	-0.1106	1365.00	0.5965	0.864243	-0.2804	1255.54
0.1983	0.938736	-0.1457	1353.35	0.6594	0.851677	-0.2746	1238.78
0.2424	0.930863	-0.1707	1343.26	0.6912	0.845142	-0.2607	1229.99
0.2929	0.921779	-0.2001	1331.54	0.7491	0.833115	-0.2306	1213.69
0.3522	0.910875	-0.2233	1317.33	0.8475	0.812305	-0.1697	1185.30
0.4048	0.901126	-0.2463	1304.51	0.8946	0.802071	-0.1259	1171.30
0.4497	0.892629	-0.2575	1293.35	0.9443	0.791125	-0.0727	1156.13

quantities κ_S^E , u^E , and α_S^E . The data were fitted by unweighted least-squares polynomial regression to the equation

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

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-test¹³ 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

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

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

Mixtures of 2-propanone, aniline, *N*-methylaniline, or pyridine with a given alkane are characterized by strong interactions between the corresponding polar molecules. This is supported by the following features. (i) The mentioned systems show miscibility gaps in such a way that the coexistence curves of the liquid–liquid equilibria have an upper critical solution temperature (UCST). For the aniline + hexane mixture, the UCST is 342.7 K,¹⁴ and it is 343.11 K¹⁵ for the heptane solution. In the case of the pyridine systems, the UCSTs are (252.2 and 255.2) K, for the mixtures with hexane and heptane, respectively.¹⁶ If one takes into account that aniline, *N*-methylaniline, and pyridine are primary, secondary, and tertiary amines, respectively, and that aniline and *N*-methylaniline are self-

associated via H-bonds, the critical temperatures given above reveal that the strength of amine–amine interactions decreases in the sequence: aniline > *N*-methylaniline > pyridine. For the 2-propanone + heptane mixture, UCST = 245.22 K.¹⁷ (ii) Large excess molar enthalpies, H^E , are as indicated by the following values for heptane systems: $H^E(\text{pyridine})^{18} = 1735 \text{ J}\cdot\text{mol}^{-1}$ and $H^E(2\text{-propanone})^{19} = 1704 \text{ J}\cdot\text{mol}^{-1}$. (iii) Positive excess molar volumes, V^E , reveal that the disruption upon mixing of amine–amine or ketone–ketone interactions is predominant over other effects which contribute negatively to V^E (structural effects arising from interstitial accommodation of one component into the other and free volume effects). For example, $V^E(\text{pyridine} + \text{heptane})^{20} = 0.2657 \text{ cm}^3\cdot\text{mol}^{-1}$, and $V^E(2\text{-propanone} + \text{heptane})^{21} = 1.130 \text{ cm}^3\cdot\text{mol}^{-1}$.

In addition to structural effects, negative V^E values of binary mixtures may be attributed to strong chemical or specific interactions between unlike molecules. For the investigated systems, the negative V^E values determined here may be due to a large extent to the mentioned interactions. The value $V^E(2\text{-propanone} + \text{aniline}) = -1.183 \text{ cm}^3\cdot\text{mol}^{-1}$ is consistent with the large negative H^E of this solution²² ($-1224 \text{ J}\cdot\text{mol}^{-1}$), which reveals strong acetone–aniline interactions. The strength of such interactions may be roughly estimated as follows. Let us denote the positive contributions to H^E from the breaking of the 2-propanone–2-propanone and aniline–aniline interactions by $\Delta H_{\text{CO-CO}}$ and $\Delta H_{\text{N-N}}$, respectively, and by $\Delta H_{\text{N-CO}}$, the negative contributions from the creation of the aniline–2-propanone interactions. Taking into account these contributions to H^E , we can write

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-Propanone (1) + Aromatic Amine (2) Mixtures

x_1	κ_S^E TPa ⁻¹	u^E m·s ⁻¹	α_P^E 10 ⁻⁶ ·K ⁻¹	x_1	κ_S^E TPa ⁻¹	u^E m·s ⁻¹	α_P^E 10 ⁻⁶ ·K ⁻¹
2-Propanone (1) + Aniline (2)							
0.0569	-20.43	40.4	-8.84	0.5501	-147.91	151.5	-101.96
0.1088	-38.63	70.7	-17.60	0.5922	-150.71	146.3	-107.09
0.1539	-53.97	92.6	-25.78	0.6499	-150.56	135.7	-111.20
0.1978	-68.26	110.2	-34.13	0.6993	-146.83	124.2	-111.56
0.2484	-83.96	126.6	-44.26	0.7522	-137.58	108.6	-107.53
0.3039	-100.14	140.4	-55.68	0.8082	-121.87	89.2	-97.67
0.3505	-112.54	148.5	-65.46	0.8533	-103.18	71.1	-84.25
0.4114	-126.55	154.4	-77.89	0.8951	-81.16	52.8	-67.19
0.4585	-135.71	156.0	-87.00	0.9545	-40.17	24.1	-33.77
0.5035	-142.74	155.0	-94.91				
2-Propanone (1) + <i>N</i> -Methylaniline (2)							
0.0440	-10.58	18.3	-6.69	0.5563	-101.86	100.2	-90.63
0.0984	-23.36	38.0	-15.97	0.6004	-103.80	97.0	-92.68
0.1447	-33.93	52.4	-24.49	0.6473	-104.40	92.4	-92.94
0.1996	-46.09	67.1	-35.09	0.6962	-102.29	85.5	-90.62
0.2503	-56.75	78.2	-45.01	0.7506	-96.46	75.6	-84.65
0.2919	-65.36	86.1	-53.12	0.8009	-87.21	64.3	-75.58
0.3511	-76.19	94.0	-64.07	0.8518	-73.81	51.1	-62.79
0.3924	-82.84	97.7	-71.02	0.8986	-56.69	37.0	-47.23
0.4520	-91.51	101.1	-79.97	0.9488	-32.34	19.8	-26.30
0.4948	-96.68	101.8	-85.28				
2-Propanone (1) + Pyridine (2)							
0.0514	-9.99	13.0	-2.43	0.5448	-65.42	55.7	-50.73
0.0969	-18.39	22.9	-6.47	0.5940	-65.25	53.3	-49.91
0.1486	-27.19	32.3	-12.46	0.6454	-63.91	50.1	-47.38
0.2023	-35.60	40.4	-19.63	0.6971	-60.56	45.5	-43.00
0.2444	-41.61	45.5	-25.47	0.7518	-55.39	39.8	-36.84
0.2960	-48.11	50.3	-32.38	0.8049	-48.27	33.2	-29.58
0.3544	-54.32	54.1	-39.36	0.8456	-41.20	27.4	-23.44
0.3965	-58.19	56.0	-43.68	0.8955	-30.58	19.5	-15.57
0.4516	-61.95	56.9	-47.80	0.9456	-17.40	10.6	-7.72
0.5036	-64.26	56.6	-50.09				

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

system ^b	T/K	property F^E	A_0	A_1	A_2	A_3	$\sigma(F^E)$
2-propanone + aniline	293.15	V^E	-4.541	-1.58	-0.34		0.008
		V^E	-4.731	-1.614	-0.31		0.005
	298.15	u^E	620.66	-88.3	40.7	-28.6	0.10
		κ_S^E	-569.04	-278.8	-98.9	-27.8	0.09
		α_P^E	-377.64	-337.6	-113.8		0.10
2-propanone + <i>N</i> -methylaniline	303.15	V^E	-4.905	-1.85	-0.42		0.008
		V^E	-2.760	-0.754	-0.22		0.004
	293.15	V^E	-2.908	-0.801	-0.19		0.004
		u^E	407.00	-13.5	14.8		0.11
		κ_S^E	-388.4	-204.4	-83.9	-31	0.14
2-propanone + pyridine	303.15	V^E	-343.32	-211.97	-10.1		0.05
		V^E	-3.106	-0.907	-0.20		0.005
	293.15	V^E	-0.922	-0.271	-0.096		0.002
		V^E	-1.003	-0.296			0.002
		u^E	226.71	-32.2	11.9		0.07
298.15	κ_S^E	-256.76	-69.8	-18.5	-5.3	0.08	
	α_P^E	-200.09	-59.6	125.0	6.1	0.04	
	V^E	-1.090	-0.317			0.003	

^a $F^E = V^E$; units, cm³·mol⁻¹. $F^E = u^E$; units, m·s⁻¹. ^b $F^E = \kappa_S^E$; units, TPa⁻¹. $F^E = \alpha_P^E$; units, 10⁻⁶·K⁻¹.

$$H^E = \Delta H_{\text{CO-CO}} + \Delta H_{\text{N-N}} + \Delta H_{\text{N-CO}} \quad (9)$$

This equation has been widely applied.^{23,24} It can be extended to $x_1 \rightarrow 0$ ²⁵ to evaluate $\Delta H_{(\text{N-CO})\text{bond}}$, the strength of the H-bonds between aniline and 2-propanone. In such a case, $\Delta H_{\text{CO-CO}}$ and $\Delta H_{\text{N-N}}$ can be replaced by $H_1^{E,\infty}$ (partial excess molar enthalpy at infinite dilution of the first component) of 2-propanone or aniline + heptane systems. So

$$\begin{aligned} \Delta H_{(\text{N-CO})\text{bond}} &= H_1^{E,\infty}(\text{aniline} + 2\text{-propanone}) - \\ &H_1^{E,\infty}(\text{aniline} + \text{heptane}) - H_1^{E,\infty}(2\text{-propanone} + \text{heptane}) \end{aligned} \quad (10)$$

The data used in this work are: $H_1^{E,\infty}(2\text{-propanone} + \text{heptane})$ ²⁶ = 9.84 kJ·mol⁻¹; $H_1^{E,\infty}(\text{aniline} + 2\text{-propanone})$ ²² = -5.68; and $H_1^{E,\infty}(\text{aniline} + \text{heptane})$ ²⁷ = 15 kJ·mol⁻¹. Therefore,

$\Delta H_{(\text{N-CO})\text{bond}} = -30.52$ kJ·mol⁻¹. This value is even lower than that for the H-bonds between 1-alkanol molecules, which in the ERAS model is assumed to be^{27,28} -25.1 kJ·mol⁻¹.

Mixtures such as amine + 1-alcohol, or + CHCl₃, characterized also by strong interactions between unlike molecules,^{28,29} show V^E values similar to those given in Table 2. So, $V^E(1\text{-propanol} + \text{propylamine})$ ³⁰ = -1.315 cm³·mol⁻¹, and $V^E(\text{trichloromethane} + \text{butylamine})$ ³¹ = -0.368 cm³·mol⁻¹. The negative ($\partial V^E/\partial T$)_P and κ_S^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.^{31,32}

On the other hand, it is remarkable that the composition dependence of the V^E and κ^E_S 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-propanone (the smaller component) and show a minimum at $x_1 = 0.6$. The fact that the H^E curve of the 2-propanone + aniline system also shows a minimum at $x_1 = 0.55$ suggests that structural effects are rather weak.

Finally, it is noticeable that V^E and κ^E_S increase in the same sequence: aniline < *N*-methylaniline < pyridine (Figures 1 and 2). This may be interpreted assuming that the new 2-propanone–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.

Conclusions

In this work, we have determined V^E , u^E , α^E_P , and κ^E_S . The V^E and κ^E_S magnitudes are negative and increase in the sequence: aniline < *N*-methylaniline < pyridine. The corresponding curves are shifted toward higher mole fractions of 2-propanone. The data have been interpreted in terms of acetone–amine interactions and weak structural effects. The existence of strong 2-propanone–amine interactions is supported by negative $(\partial V^E/\partial T)_P$ values and by the enthalpy of 2-propanone–aniline association which is more negative than that of the H-bonds between 1-alcohol molecules.

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