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

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ABSTRACT

Densities, ρ, and speeds of sound, u, of 2-propanone + 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, and the excess functions at 298.15 K for the thermal expansion coefficient, α_P^E, and for the isentropic compressibility, K_S^E at 298.15 K. V^E, K_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 which are more important in the former solutions. From the comparison with similar data obtained for 2-propanone + aniline, + *N*-methylaniline, or + pyridine systems, it is concluded that interactions between unlike molecules are stronger in mixtures containing aromatic amines. Free volume effects are present in solutions with dipropyl or dibutylamine as the V^E curves are shifted towards higher mole fractions of 2-propanone.

1. 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]. 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]. So, the aqueous solution of dimethylformamide is a model solvent representing the environment of the interior of proteins. Amides have many 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 then pertinent in order to gain insight into amide solutions. In this article, we report densities, speeds of sound and excess molar volumes at 293.15 K, 298.15 K and 303.15 K, and the excess functions at 298.15 K for the isobaric thermal expansion coefficients and the isentropic compressibility for the mixtures 2-propanone + dipropylamine, + dibutylamine or + triethylamine. In the first work of this series we have provided similar data for 2-propanone + aniline, + *N*-methylaniline, or + pyridine [4].

2. Experimental

2.1. Materials

2-Propanone (≥0.995) was from Sigma Aldrich; dipropylamine (≥0.99) and dibutylmaine (≥0.995) were from Aldrich and triethylamine (≥0.995) was from Fluka 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).

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 [5].

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Table 1
Physical properties of pure compounds, 2-propanone, 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.

Property	T/K	2-propanone		Dipropylamine		Dibutylamine		Triethylamine	
		Exp.	Lit	Exp.	Lit	Exp.	Lit.	Exp.	Lit.
ρ/g cm^3	293.15	0.790546	0.78998[a]	0.738301	0.73720[b]	0.759591	0.762022[c]	0.727514	0.7276[a] 0.72753[d]
	298.15	0.784868	0.784431[e] 0.78428[h] 0.78457[k]	0.733676	0.73336[f] 0.73368[g] 0.73333 [l]	0.755549	0.75553[f] 0.75570[i] 0.75572[g] 0.75595[j]	0.722892	0.72318[g] 0.72376[j]
	303.15	0.779169	0.77914[h]	0.729102	0.72820[b] 0.73121[j] 0.73019[m]	0.751481	0.75194[j] 0.75248 [m]	0.718332	0.71836[d]
u/m s^{-1}	293.15	1182.5	1192[k]	1209.1		1261.3	1269.47[c]	1132.7	
	298.15	1160.4	1161.72[e] 1154[h] 1160.6[n]	1187.8	1198[j]	1241.4	1248[j] 1246.7[c]	1111.2	1123[j] 1115.1[o]
	303.15	1139.2	1131.2[h]	1167.4	1174[j]	1222.6	1227[j]	1091.1	1101[j]
α_p/10^{-3} K^{-1}	298.15	1.45	1.426[h]	1.25	1.201[j]	1.07	1.059[j]	1.27	1.24[o]
κ_s/Tpa^{-1}	293.15	904.66		926.5		827.6	814.31[c]	1071.29	
	298.15	946.29	944.59[e] 958[h] 946[n]	966.1	947[j]	858.8	849[j]	1120.39	1113[o]
	303.15	988.80	1003[h]	1006.4	992[j]	890.2	883[j]	1169.44	1135[j]
κ_T/Tpa^{-1}	298.15	1317.5	1324[a] 1330[h]	1221.8	1183[j]	1053.4	1039[j]	1432.2	1404[o]
C_p/J mol^{-1} K^{-1}	298.15		124.9[a]		252.84[a]		302[j]		216.43[p]

[a] [6]; [b][32]; [c][33]; [d][34]; [e][17]; [f][35]; [g][21]; [h][36]; [i][37]; [j][38]; [k][39]; [l][40]; [m][41]; [n][42]; [o][43]; [p][44].

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. The calibration of the apparatus was carried out with deionised 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 are $\pm 1\cdot 10^{-2}$ 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 [9–12]. The accuracy in V^E is believed to be less than $\pm(0.01|V^E_{\max}| + 0.005)\text{cm}^3\text{mol}^{-1}$, where $|V^E_{\max}|$ denotes the maximum experimental value of the excess molar volume with respect to the mole fraction.

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, $\alpha_P = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right)_P$ 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 property, F, are calculated using the equations [9,13]:

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

and

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

where C_p is the isobaric heat capacity, $\phi_i = \frac{x_iV_i}{V^{id}}$ the volume fraction, κ_T, the isothermal compressibility, and F_i, the F value of component i, respectively. For κ_S the ideal values are calculated according to [13]:

$$\kappa_S^{id} = \kappa_T^{id} - \frac{TV^{id}\alpha_P^{id2}}{C_P^{id}} \tag{4}$$

In this work, we have determined the excess functions:

$$F^E = F - F^{id} \tag{5}$$

for $F = V^E$, κ_s and α_P

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-propanone. Table 3 contains the derived quantities κ_S^E and α_P^E. The data were fitted by unweighted least-squares polynomial regression to the equation:

$$F^E = x_1(1-x_1)\sum_{i=0}^{k-1} A_i(2x_1-1)^i \tag{6}$$

where F stands for the properties cited above. The number of coefficients k used in Eq. (6) 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:

$$\sigma\left(F^E\right) = \left[\frac{1}{N-k}\sum\left(F^E_{cal} - F^E_{exp}\right)^2\right]^{1/2} \tag{7}$$

where N is the number of direct experimental values. Results on V^E and κ_S^E are shown graphically in Figs. 1 and 2. No data have been encountered in the literature for comparison.