



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

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ABSTRACT

Densities, ρ , and speeds of sound, u , of {2-heptanone + dipropylamine (DPA), +dibutylamine (DBA), or +triethylamine (TEA)} 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_m^E , 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 . Structural effects increase with the ketone size in mixtures with a fixed amine. V_m^E , κ_S^E , and α_p^E increase when DPA is replaced by DBA in systems with a given ketone as: (i) interactions between unlike molecules are more easily created in solutions containing the shorter amines; (ii) this effect predominates over that related to the disruption of the amine–amine interactions. Contributions to V_m^E from the creation of interactions between unlike molecules and from the breaking of the amine–amine interactions are both lower in absolute value for TEA systems when are compared to those of DPA solutions. The increasing positive V_m^E values observed when DPA is replaced by TEA in solutions with propanone or 2-butanone reveal that the former contribution is less relevant, and more important for the DPA mixtures. The opposite behavior for 2-heptanone systems is attributed to the existence of structural effects when this ketone is mixed with TEA. These general trends are confirmed by the treatment of the mixtures using the PFP theory, and the internal pressure concept.

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1. Introduction

The investigation of liquid mixtures involving the amide functional group is necessary for a better knowledge of complex molecules of biological interest [1]. Thus, the aqueous solution of dimethylformamide is a model solvent representing the environment of the interior of proteins, which are polymers of amino acids linked to each other by the very common in nature peptide bonds. Amides have also many practical applications. Dimethylformamide and *N*-methylpyrrolidone are used as highly selective extractants for the recovery of aromatic and saturated hydrocarbons from petroleum feedstocks [2], 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 ρ , u , and V_m^E data at (293.15, 298.15, and 303.15) K, and u^E , α_p^E , and κ_S^E at 298.15 K for the mixtures {2-heptanone + dipropylamine (DPA), +dibutylamine (DBA),

or +triethylamine (TEA)}. Previously, we have provided similar data for systems containing propanone, or 2-butanone with the same amines [3,4], as well as for the mixtures (propanone, 2-butanone, or 2-heptanone + aniline, +*N*-methylaniline, or +pyridine) [5–7]. Data at 298.15 K on ρ , u , and V_m^E for the (2-butanone + diethylamine) system are available in the literature [8].

2. Experimental

2.1. Materials

2-Heptanone (≥ 0.99) was from Sigma Aldrich; dipropylamine (≥ 0.99) and dibutylamine (≥ 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 cm³. Caution was taken to prevent evaporation, and the

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TABLE 1

Physical properties of pure compounds, 2-heptanone, 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-Heptanone		Dipropylamine		Dibutylamine		Triethylamine	
		This work	Literature	This work	Literature	This work	Literature	This work	Literature
$\rho/(\text{g} \cdot \text{cm}^3)$	293.15	0.815433	0.81537 ^a	0.738259	0.73720 ^b	0.759529	0.762022 ^c	0.727333	0.7276 ^a 0.72753 ^d
	298.15	0.811139	0.81123 ^a 0.8111 ^g	0.733810	0.73336 ^e 0.73368 ^f	0.755577	0.75553 ^e 0.75570 ^f 0.75572 ^f 0.75595 ⁱ	0.722729	0.72318 ^f 0.72376 ⁱ
	303.15	0.806827			0.72820 ^b 0.73121 ⁱ 0.73019 ⁱ	0.751407	0.75194 ⁱ 0.75248 ^f	0.718092	0.71836 ^d
$u/(\text{m} \cdot \text{s}^{-1})$	293.15	1281.92		1209.38		1261.23	1269.47 ^c	1132.47	
	298.15	1262.49	1270.7 ^a	1188.00	1198 ⁱ	1241.38	1248 ⁱ 1246.7 ^c	1110.9	1123 ^j 1115.1 ^k
	303.15	1244.14		1167.57	1174 ⁱ	1222.21	1227 ⁱ	1090.65	1107 ⁱ
$\alpha_p/(10^{-3} \text{K}^{-1})$	298.15	1.06	1.06 ^a	1.24	1.201 ⁱ	1.07	1.059 ^j	1.28	1.24 ^k
κ_S/TPa^{-1}	293.15	746.26		926.11		827.69	814.31 ^c	1072.04	
	298.15	773.48	763.43 ^a	965.57	947 ⁱ	858.85	849 ⁱ	1121.18	1113 ^k
	303.15	800.71		1006.02	992 ⁱ	890.91	883 ⁱ	1170.7	1135 ⁱ
κ_T/TPa^{-1}	298.15	968.27	957 ^a	1215.1	1183 ⁱ	1054.0	1039 ⁱ	1436.5	1404 ^k
$C_{p,m}/(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$	298.15		242.54 ^l		252.84 ^a		302 ⁱ		216.43 ^m

^a [10].^b [52].^c [53].^d [54].^e [55].^f [35].^g [56].^h [57].ⁱ [58].^j [59].^k [60].^l [61].^m [62].

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 1995 issued by IUPAC [9].

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 thermostated within ± 0.01 K. The calibration of the apparatus was carried out with deionised double-distilled water, hexane, heptane, octane, isooctane, cyclohexane, and benzene, using ρ values from the literature [10–13]. The uncertainty for the ρ and u measurements are $\pm 1 \cdot 10^{-2} \text{ kg} \cdot \text{m}^{-3}$ and $\pm 0.1 \text{ m} \cdot \text{s}^{-1}$, respectively, and the corresponding precisions are $\pm 1 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$ and $\pm 0.01 \text{ m} \cdot \text{s}^{-1}$. The experimental technique was checked by determining V_m^E and u of the standard mixtures: (cyclohexane + benzene) at the temperatures (293.15, 298.15, and 303.15) K and (cyclohexane + hexane) and (2-ethoxyethanol + heptane) at 298.15 K. Our results agree well with published values [13–16]. The uncertainty in V_m^E is believed to be less than $\pm(0.01|V_{\text{max}}^E| + 0.005) \text{ cm}^3 \cdot \text{mol}^{-1}$, where $|V_{\text{max}}^E|$ denotes the maximum experimental value of the excess molar volume with respect to the mole fraction. The uncertainty of the deviations of u from the ideal behavior is estimated to be $0.3 \text{ m} \cdot \text{s}^{-1}$.

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,

$\alpha_p = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p$ 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:

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

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 [13,17]:

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

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, $\phi_i = \frac{x_i V_{m,i}}{V_m^{id}}$ 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 [13]:

$$\kappa_S^{id} = \kappa_T^{id} - \frac{TV_m^{id} \alpha_p^{id2}}{C_{p,m}^{id}} \quad (4)$$

and

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

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