J. Chem. Thermodynamics 90 (2015) 158–168

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Thermodynamics of mixing for binary mixtures of 1-octanol and 1-decanol with n-dodecane and ternary mixture of (TBP + 1-octanol + dodecane) at T = (298.15 to 323.15) K

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ARTICLE INFO

Article history:
Received 19 January 2015
Received in revised form 10 June 2015
Accepted 13 June 2015
Available online 2 July 2015

Keywords:
Density
Speed of sound
Excess parameters
Tributyl phosphate
Dodecane
Alcohols

ABSTRACT

Densities (ρ) and speed of sound (u) of the binary mixtures of 1-octanol and 1-decanol with dodecane and ternary mixture of {1-octanol + tributyl phosphate (TBP) + dodecane} were measured at temperatures from (298.15 to 323.15) K over the entire composition range and at atmospheric pressure. Using these experimentally determined quantities, the excess molar volume (V^E), excess isentropic compressibility (κ_S^E) for the binary mixtures and internal pressure (p_i) of (alcohol + dodecane) binary mixtures have been calculated. The deviations shown by the excess quantities have been interpreted in terms of intermolecular interactions and structure of components. Using Hildebrand regular solution theory, several other parameters like the enthalpy and entropy of mixing of the binary components have been obtained. From acoustic measurements, the probable dimerization constant of the alcohols has also been determined. The values of these parameters give an indication of the subtle structural changes that occur in these binary mixtures.

1. Introduction

1-Alkanol + n-alkanes are interesting systems for study because of the hydrogen bond association of the 1-alkanol molecules. This association is known to give rise to strong non-ideality even in the alkane-rich regions. The hydrogen bonding sufficiently influences the extent of packing amongst the alcohol and alkane molecules and this will have a definite impact on the excess volume and compressibility of these binary mixtures. The study of alcohol-alkane mixtures is also important in various fields of science and technology, one very prominent among them being the field of separation science related to nuclear fuels. During reprocessing of nuclear fuels the organic phase often splits into two phases and this phenomenon is known as third-phase formation. This is quantified in terms of limiting organic concentration (LOC) of the metal ion in the organic phase, above which the third-phase starts appearing. This phenomenon creates various problems for the associated hydrometallurgical operations involved during reprocessing and therefore its occurrence should be prevented. The LOC value is known to increase considerably in presence of polar compounds like long-chain alcohols [1]. This aspect necessitates thermodynamic study of mixtures of long-chain alcohols with other components involved in the process of solvent extraction since the mixing properties help to determine the nature of interactions among these components.

In our previous work, we have elucidated the nature of interactions between extractant-diluent and extractant-modifier binary systems from the excess mixing properties like volume and compressibility [2,3]. In this study, we report the excess properties of mixing of 1-octanol and 1-decanol with dodecane. Although many studies have been done on (1-alkanol + n-alkane systems) [4–8], to the best of our knowledge, no report exists for the temperature-dependent study of mixing properties of 1-octanol and 1-decanol with dodecane.

We have measured the density and sound speed of binary mixtures of 1-octanol and 1-decanol with dodecane and correlated the nature of interaction present among these molecules with the excess thermodynamic properties like volume and isentropic compressibility. From the measurement of the sound speed and density, we have also calculated the partial molar excess parameters for TBP and octanol for the ternary mixture (octanol + dodecane + TBP), aiming at interpreting molecular interactions in this ternary system. Using the regular solution model, as

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http://dx.doi.org/10.1016/j.jct.2015.06.029
0021-9614/

proposed originally by Hildebrand, [9] the partial enthalpy of mixing of the components for the (alcohol + dodecane) binary mixtures has been determined and suitability of application of this theory to these systems has been assessed.

2. Experimental

2.1. Chemicals

The TBP was purchased from E. Merck, Germany. The 1-octanol and 1-decanol were purchased from Kemphasol and dodecane was purchased from Otto Chemie Pvt. Ltd. All these chemicals were used as received. Sample provenance, purity, water content and other details regarding the purchased chemicals are summarized in table 1.

2.2. Equipment and procedure

Two sets of binary mixtures of 1-octanol and 1-decanol with dodecane were prepared with the mole fraction of the alcohol ($x_{Octanol}/x_{Decanol}$) varying from 0.05 to 0.95 in each case. For the ternary mixtures of (TBP + octanol + dodecane), the compositions were chosen in such a way that they span the entire ternary composition space. The liquid mixtures were prepared by weight using a Mettler balance with an accuracy of ±0.0001 g. The density and sound speed of all these binary and ternary mixtures as well as the pure compounds were measured within the temperature range of (298.15 to 323.15) K (temperature measurement repeatability being ±0.001 °C) in an automated density and sound velocity metre (Model: DSA 5000 M) having a density measurement repeatability of 0.000005 $g \cdot cm^{-3}$ and sound speed measurement repeatability of 0.5 $m \cdot s^{-1}$. The instrument operates at the ultrasonic frequency of 3 MHz. The density and sound speed values of doubly distilled water were compared with those provided in the instruction manual of the instrument. For the density value, the agreement is better than 0.01% and for the sound velocity the agreement is around 0.07%. The experimental values of density and sound speed of the pure components at different temperatures, along with literature values [10–15], are tabulated in table 2. It is seen that barring a few values, where the deviation is slightly higher, the agreement between the experimental and literature values are approximately within 0.1%. The uncertainty obtained in the derived quantities, namely, excess molar volume (V^E) and excess isentropic compressibility (κ_s^E) from density and sound speed measurements are within $5 \cdot 10^{-10}\ m^3 \cdot mol^{-1}$ and $0.1 \cdot 10^{-11}\ m^2 \cdot N^{-1}$ respectively. For the sake of comparison, our density, sound speed and excess molar volume values for the (alcohol + dodecane) binary systems have been plotted along with literature data [33–35] at T = (298.15 and 308.15) K and are shown in figures 1a–1c. There is a systematic variation of 1 $kg \cdot m^{-3}$ in the density value which is due to presence of water impurity in the alcohol samples. In figure 1c, we have plotted our excess molar volume data with and without taking into consideration the water impurity in the alcohol. The correction for water impurity has been done as follows.

The density of pure alcohol was corrected by considering the amount of water impurity (as given in table 1) in the alcohol samples. Using this corrected density and considering the water impurity in dodecane to be negligible as compared to that in alcohols, the excess volume was calculated using the following formula:

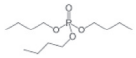
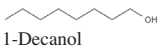
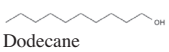
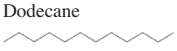
$$V^E = (x_1' M_1 + x_2 M_2 + x_3 M_3)/\rho - (x_1' M_1/\rho_1') - (x_2 M_2/\rho_2) - (x_3 M_3/\rho_3)$$

TABLE 2
Comparison of experimentally measured densities, ρ and ultrasonic speeds, u of pure components with literature values at T = 298.15 K and higher temperatures and P = 0.1 MPa.

Component	T/K	ρ/kg · m^{-3}		u/m · s^{-1}	
		Exp	Lit	Exp	Lit
Doubly distilled water	298.15	997.04	997.043	1498	1497.00
Tributyl phosphate (TBP)	298.15	972.82	972.70[a], 972.49[b]	1265	
	303.15	968.50	968.19(303.17 K)[b]		
	308.15	964.18	963.88(308.19 K)[b]		
	313.15	959.86	959.70(313.05 K)[b]		
	318.15	955.53	955.37(318.07 K)[b]		
	323.15	951.20	951.30(322.8 K)[b]		
1-Octanol	298.15	822.28	821.18[c], 821.83[d]	1348	1348[c], 1348[d]
	303.15	818.79	818.23[d]	1331	1338[d]
	308.15	815.27	814.74[d]	1314	1314[d]
	313.15	811.73	810.10[d]	1297	1298[d]
1-Decanol	298.15	827.21	826.64[c], 826.76[d]	1380	1380[c], 1380[d]
	303.15	823.76	822.85[d]	1365	1363[d]
	308.15	820.31	819.43[d]	1346	1346[d]
	313.15	816.83	815.98[d]	1329	1329[d]
Dodecane	298.15	745.62	744.90[e], 745.17[f]	1279	1278[e]
	303.15	741.98	741.27[e]	1259	1259[e]
	308.15	738.34	737.95[f]	1240	1240[f]
	318.15	731.03	730.69[f]	1203	1202[f]

Standard uncertainty in density $u(\rho)$ = 1 $kg \cdot m^{-3}$.
Standard uncertainty in sound speed $u(u)$ = 0.5 $m \cdot s^{-1}$.
Standard uncertainty in temperature $u(T)$ = 0.001 K.
Standard uncertainty in pressure $u(P)$ = 1 kPa.
[a] Reference [10].
[b] Reference[11].
[c] Reference[12].
[d] Reference[13].
[e] Reference[14].
[f] Reference[15].

TABLE 1
Sample provenance, purity and structure.

Chemical name and structure	CAS No	Source	Water content[a] · 10^6	Purificatin method	Mass fraction purity[b]
Tributyl phosphate 	126-73-8	E. Merck, Germany	4300	As received	0.99
1-Octanol 	111-87-5	Kemphasol	5190	As received	0.989
1-Decanol 	112-30-1	Kemphasol	4875	As received	0.99
Dodecane 	112-40-3	Otto Chemie Pvt. Ltd	30	As received	0.99

[a] Determined by Karl Fishcer titration.
[b] As declared by manufacturer.