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Thermochimica Acta 454 (2007) 99–108
thermochimica acta
www.elsevier.com/locate/tca

Thermodynamic study of the *n*-octane-1-pentanol-sodium dodecyl sulfate solutions in water

Nikolai G. Polikhronidi [a], Genadii V. Stepanov [a], Ilmutdin M. Abdulagatov [b,*], Rabiyat G. Batyrova [a]

[a] *Institute of Physics of the Dagestan Scientific Center of the Russian Academy of Sciences, 367005 Makhachkala, M. Yaragskogo Str. 94, Dagestan, Russia*
[b] *Institute for Geothermal Problems of the Dagestan Scientific Center of the Russian Academy of Sciences, 367003 Makhachkala, Shamilya Str. 39-A, Dagestan, Russia*

Received 1 August 2006; received in revised form 12 December 2006; accepted 17 December 2006
Available online 22 December 2006

Abstract

The thermodynamic properties, $PVTx$ (T_S, P_S, ρ_S), $(\partial P/\partial T)_{VX}$, and $C_V VTx$, of three microemulsions (water + *n*-octane + sodium dodecylsulfate + 1-pentanol) with composition of solution-1: 0.0777 (H_2O):0.6997 (*n*-C_8H_{18}):0.0777 (SDS):0.1449 (1-$C_5H_{11}OH$) mass fraction; solution-2: 0.6220 (H_2O):0.1555 (*n*-C_8H_{18}):0.0777 (SDS):0.1448 (1-$C_5H_{11}OH$) mass fraction; and solution-3: 0.2720 (H_2O):0.5054 (*n*-C_8H_{18}):0.0777 (SDS):0.1449 (1-$C_5H_{11}OH$) mass fraction were measured. Sodium dodecylsulfate (SDS) was used as an ionic surfactant, 1-pentanol used as stabilizer (cosurfactant), and *n*-octane as oil component in aqueous solution. A high-temperature, high-pressure, adiabatic, and nearly constant-volume calorimeter supplemented by quasi-static thermogram technique was used for the measurements. Measurements were made at eight densities (isochores) between 475.87 and 919.03 kg m^{-3}. The range of temperature was from 275 to 536 K and pressure range was up to 138 bar. Uncertainty of the pressure, density, derivative $(\partial P/\partial T)_{VX}$, and heat capacity measurements are estimated to be 0.25%, 0.02%, 0.12–1.5%, and 2.5%, respectively. Temperatures at liquid–gas phase transition curve, $T_S(\rho)$, for each measured densities (isochores) were determined using a quasi-static thermogram technique. The uncertainty of the phase transition temperature measurements is about ±0.02 K. The effect of temperature, density, and concentration on the heat capacity of the microemulsions is discussed. Along the isochore of 438.40 kg m^{-3} at temperatures above 525.44 K for the first solution the precipitation of the solid phase (SDS) was found.

Keywords: Adiabatic calorimeter; Density; Heat capacity; *n*-Octane; 1-Pentanol; Phase transition; Pressure; Sodium dodecylsulfate; Water

1. Introduction

Aqueous solutions containing the surfactant are important for many practical applications. For example, the surfactants are used for the enhanced oil recovery and detergency and improving the understanding of surfactants effect on this process have practical importance. The modeling and prediction of the process of tertiary oil recovery or the condition of the solubilization of hydrocarbons in ternary systems generally formed with water, a surfactant (SDS), and a cosurfactant (alcohol) are required knowledge accurate thermodynamic properties and phase diagram data for quaternary system, microemulsion (water + surfactant (SDS) + alcohol + hydrocarbon). Microemulsion systems are very important in biology, medicine, and environment, and in tertiary oil recovery processes [1–5]. Less attention has been paid to the thermodynamic of the solutions with surfactant on the especially direct measurements of the different properties as functions of concentration, temperature, and pressure. Volumetric and calorimetric data are great important since they can be used test theories and models and to obtain information on the interaction governing the micelles formation in different liquid media.

Isochoric heat capacity is one of the important thermodynamic characteristics of fluids and fluid mixtures in phase transition phenomena study. Constant-volume calorimeter provides a useful method for the study of phase transition

* Corresponding author. Present address: Physical and Chemical Properties Division, National Institute of Standards and Technology, 325 Broadway, Boulder, CO 80305, USA. Tel.: +1 303 497 4027; fax: +1 303 497 5224.
E-mail address: ilmutdin@boulder.nist.gov (I.M. Abdulagatov).

0040-6031/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2006.12.014

phenomena in complicated multicomponent solutions. In this work, we use the fact that a constant-volume heat capacity C_V is a very sensitive indicator of phase changes [6–17]. Therefore, the constant-volume heat capacity C_V can be a very sensitive tool that determines various type liquid–solid (L–S), liquid–liquid (L–L), liquid–vapor (L–V), solid–vapor (S–V), liquid–solid–vapor (L–S–V), liquid–liquid–solid (L–L–S), and liquid–liquid–vapor (L–L–V) phase transitions occurring in a complex fluid mixtures heated in a closed volume. The discontinuity in C_{VX} behavior at the intersection of the phase boundary curve are connected with various type phase transitions (L–L, L–V, L–S, V–S, L–L–S, L–L–V, and L–S–V) occurring in a complicated fluid mixtures heated in a closed volume. Isochoric heat capacity C_V measurements improve our understanding of many important phenomena taking place in complex multicomponent mixtures near the phase transition points. Isochoric heat capacity experiments enable one to accurately determine the phase transition temperatures T_S of the system from the one- to the two-phase, from the two- to the three-phase state and vice versa [18,19]. The technique of determining phase boundary parameters (T_S, P_S, ρ_S, x) (L–V, L–L–V, and L–V–S) is described in our previous publications [6–17]. Fig. 1 shows schematic representation of the general behavior of isochoric heat capacity C_V as a function of specific volume V at fixed sub-critical isotherm ($T<T_C$) in the vapor (one-phase), liquid (one-phase), and vapor–liquid (two-phase) phases. The heat capacity C_V jumpily decreases or increases on passing through the phase transition points while heating isochorically. Thus, the phase transition observed can mark only the disappearance one of the phase (vapor, liquid, solid) (L–V ⇔ L, L–V ⇔ V, L–G–V ⇔ L–V, L–V–S ⇔ L–S, L–V–S ⇔ V–S). At the phase transition, the density of the liquid solution is readily calculated from the volume of the calorimeter and the mass of the solution (see below). This technique will be used in this work to study the two-phase (L–V) boundaries for the complex quaternary mixtures of water + *n*-octane + SDS + 1-pentanol. Some authors have used a break-point technique (*P–V* and *P–T* break points) in a *PVTx* experiment to study phase boundary curves in aqueous salt solutions (see for example [20–22]). While this method can be quite reliable, its precision can be improved upon by applying a sensitive calorimetric technique.

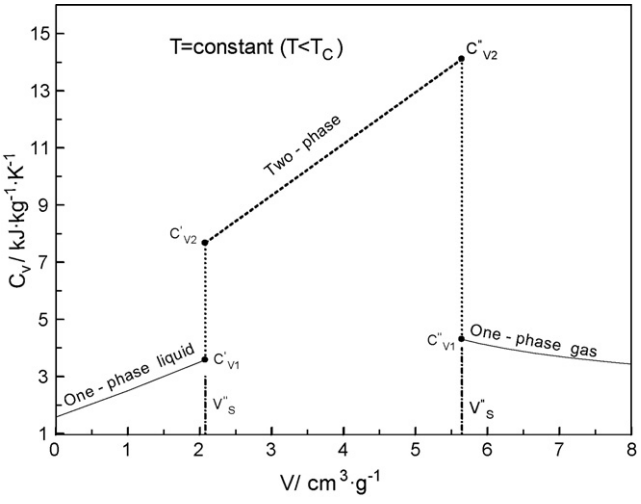

Fig. 1. Typical isochoric heat capacity behavior as a function of specific volume ($V = 1/\rho$) along constant temperature ($T<T_C$). C'_{V1}: one-phase liquid isochoric heat capacity at the phase transition point, C'_{V2}: two-phase liquid isochoric heat capacity at the phase transition point, C''_{V1}: one-phase vapor isochoric heat capacity at the phase transition point, C''_{V2}: two-phase vapor isochoric heat capacity at the phase transition point, V'_S: specific volume of liquid at the liquid–gas phase transition point (saturated liquid volume), V'_S: specific volume of the gas at the liquid–gas phase transition point (saturated gas volume).

The primary objective of this work is to provide accurate experimental volumetric (*PVTx*), $(\partial P/\partial T)_{VX}$, calorimetric ($C_V VTx$), and phase boundary ($T_S$, P_S, ρ_S, x) properties data for complex quaternary fluid mixtures (microemulsion). The microemulsion has been formed by mixing water, surfactant (SDS), cosurfactant (1-pentanol), and hydrocarbon (*n*-octane), water + n-octane + SDS + 1-pentanol. In this system SDS is surfactant used as component in stabilizing the microemulsion, alcohol (1-pentanol) used as cosurfactant. As typical oil, *n*-octane was used. Surfactant favors the formation and the stabilization of alcohol microaggregates. The cosurfactant used is very essential to increase the solubilization of hydrocarbons in water. Calorimetric studies are efficient method for investigating of the microemultions and provide very useful information about microstructure of the system, to understand the mechanism of formation of different structural zones in the microemulsion phase diagram. These zones play very essential role in determination optimal conditions for the maximum solubilizing oil in water. The concentration of the surfactant and cosurfactant play also very essential role in solubilizing of oil in water. It is the purpose of this paper to accurate determine the locations of the phase boundaries (phase behavior) encountered from 275 to 536 K, as they manifest themselves in peaks and jumps in the heat capacity or isochoric *P–T* break point data for water + *n*-octane + SDS + 1-pentanol. In our previous papers [18,19] we used this technique to accurately determine the location of the L–V, L–L–V and L–S–V phase transition curves for complicated multicomponent thermodynamic systems such as water + hydrocarbon and water + salt. Fig. 2 shows the typical C_V–T curves for two complicated mixtures (partially miscible mixture H_2O + *n*-C_6H_{14} [19] and $H_2O + Na_2SO_4$ [18] solution with salt precipitation at high temperatures, type 2 aqueous solution) near the two different types of phase transition points. In Fig. 2 first and second peaks indicates the occurrence of two different type phase transitions (L–L, L–V and L–S, L–V). First peak is observed when second liquid disappears (Fig. 2a) and when salt first precipitates (Fig. 2b) and, on further heating, a second lambda-shaped peak is seen when the vapor or liquid phase disappears.

Previously some thermodynamic properties (density, heat capacity at constant pressure) for microemulsions (water + alcohol + hydrocarbon + surfactant) were studied by several authors [23–26]. The density (ρ) and heat capacity at constant pressure (C_P) of microemulsion formed by water + SDS + *n*-butanol + toluene has been studied by Roux et al. [23] and Roux-Desgranges et al. [24] at room temperature (25 °C). These properties for the ternary system (water + SDS + *n*-butanol) and (water + toluene + *n*-butanol) were studied by the same authors Roux-Desgranges et al. [25]