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Cluster/kinetic method

Mass spectrometric determination of the surface compositions of ethanol–water mixtures

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Abstract

Vapor-phase clusters from ethanol–water liquid mixtures of varying compositions, generated by sampling the binary vapor in equilibrium with the liquid mixture, were examined with the aid of a time-of-flight mass spectrometer. The variation of the mole fraction of the alcohol in the cluster beam with the liquid mole fraction was found to be identical to that of the surface concentration obtained from surface tension measurements. The results also compare well with those obtained from neutron reflection. The mass spectrometric method of determining surface compositions of liquid mixtures is more direct and model independent and is applicable over the entire range of compositions. (Int J Mass Spectrom 212 (2001) 267–271) © 2001 Elsevier Science B.V.

Keywords: Surface composition; Ethanol–water clusters; Time-of-flight mass spectrometry

1. Introduction

It is well known that in a binary liquid mixture, the component with a lower surface free-energy adsorbs at the air–solution interface, causing surface enrichment [1]. For many decades, the only experimental evidence for surface enrichment has been based on surface tension measurements. In the ethanol–water system, which has served as an excellent example of surface enhancement, the surface tension decreases sharply as the ethanol mole fraction, x_E, in the liquid reaches ~0.25, beyond which the variation is marginal [2,3]. Schofield et al. [2] and Guggenheim et al. [4] calculated the surface excess by employing the Gibbs adsorption equation, making use of the surface tension data as well as the activity values of the two components from vapor pressure data. More recently, Laaksonen [5] has estimated the surface mole fraction of ethanol assuming the surface tension of the mixture to be proportional to the surface tensions of the pure substances multiplied by their volume fractions in the surface layer. It is only relatively recently that measurements of the surface concentration were carried out in the ethanol–water system by Li et al. [6] by

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Dedicated to R. Graham Cooks on the occasion of his sixtieth birthday.

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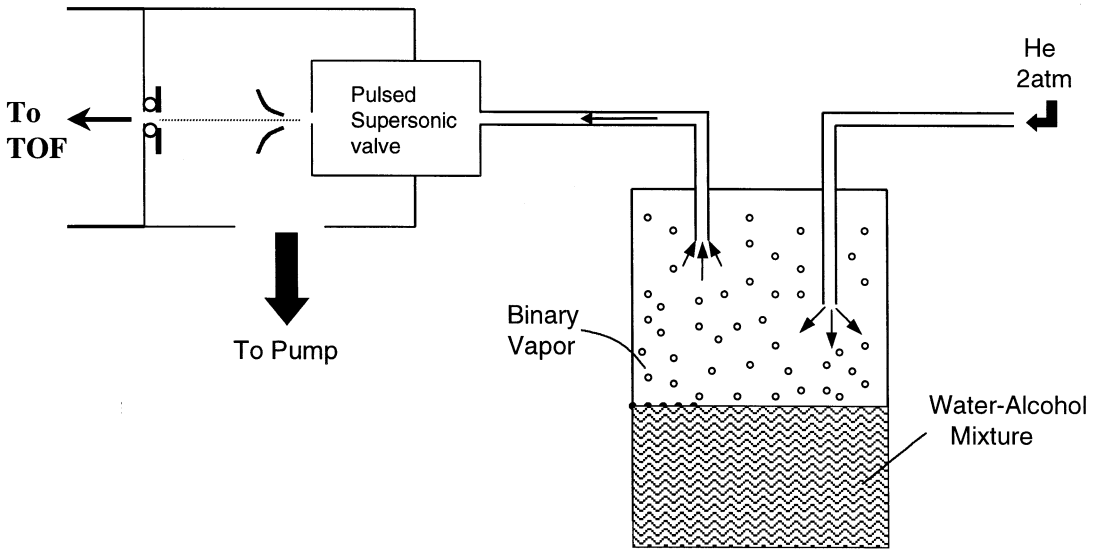

Fig. 1. Schematic of the experimental set-up: He backpressure of 2 atmospheres is applied on the water–alcohol mixture. The binary vapor produced is sampled through a pulsed supersonic valve, and the cluster beam is analyzed using the time-of-flight mass spectrometer.

employing grazing-incidence neutron reflection, commonly used to study surface enrichment in polymer blends [7]. These workers have fitted the partial structure factors from neutron diffraction data to different models of distribution of ethanol and water at the interface and compared their results with those from surface tension measurements [2,4]. The measurements of Li et al. [6] were, however, carried out over a limited range of compositions ($0 < x_E < 0.25$), and the method, besides being model dependent, suffers from poor sensitivity at higher ethanol concentrations ($x_E > 0.25$) because of the diminishing contrast between the ethanol layer and the bulk solution.

In this article, we report a simple experimental method for determining the surface composition of a liquid mixture by analyzing the binary vapor in equilibrium with the liquid surface using time-of-flight (TOF) mass spectrometry. For this purpose, we have generated a cluster beam of the binary vapor swept off the surface of the ethanol–water liquid mixture over the entire range of compositions. We show that the mole fraction of ethanol in the cluster beam corresponds almost exactly to the surface mole fraction obtained from surface tension measurements.

2. Experimental

Binary mixtures of quartz-distilled water and ethanol (HPLC grade, Aldrich, Bangalore, India) were prepared with varying molar composition spread over the entire range at intervals of ~0.1. To generate a molecular beam, 6 mL of the binary mixture was placed in a stainless steel cell connected to a pulsed supersonic valve (R.M. Jordan, California, USA) and was subjected to a helium backpressure of 2 atmospheres from the top (see schematic in Fig. 1). The ethanol–water vapor in equilibrium with the binary liquid was swept off the surface of the liquid and injected into a vacuum of 10^{-7} torr through a 0.5-mm orifice in the pulsed valve, operating at 10 Hz and 4000 Amperes. The details of this indigenous cluster apparatus are reported elsewhere [8]. Briefly, it consists of a cluster generation chamber, which is connected to a linear TOF mass spectrometer through a gate valve. A slit-skimmer assembly placed midway helps differential pumping of the two chambers. The molecular clusters were ionized using the 355-nm harmonic of a pulsed Nd-YAG laser (GCR-170) operating in the Q-switch mode (10Hz, 80 mJ/pulse). The extraction and acceleration voltages were held at

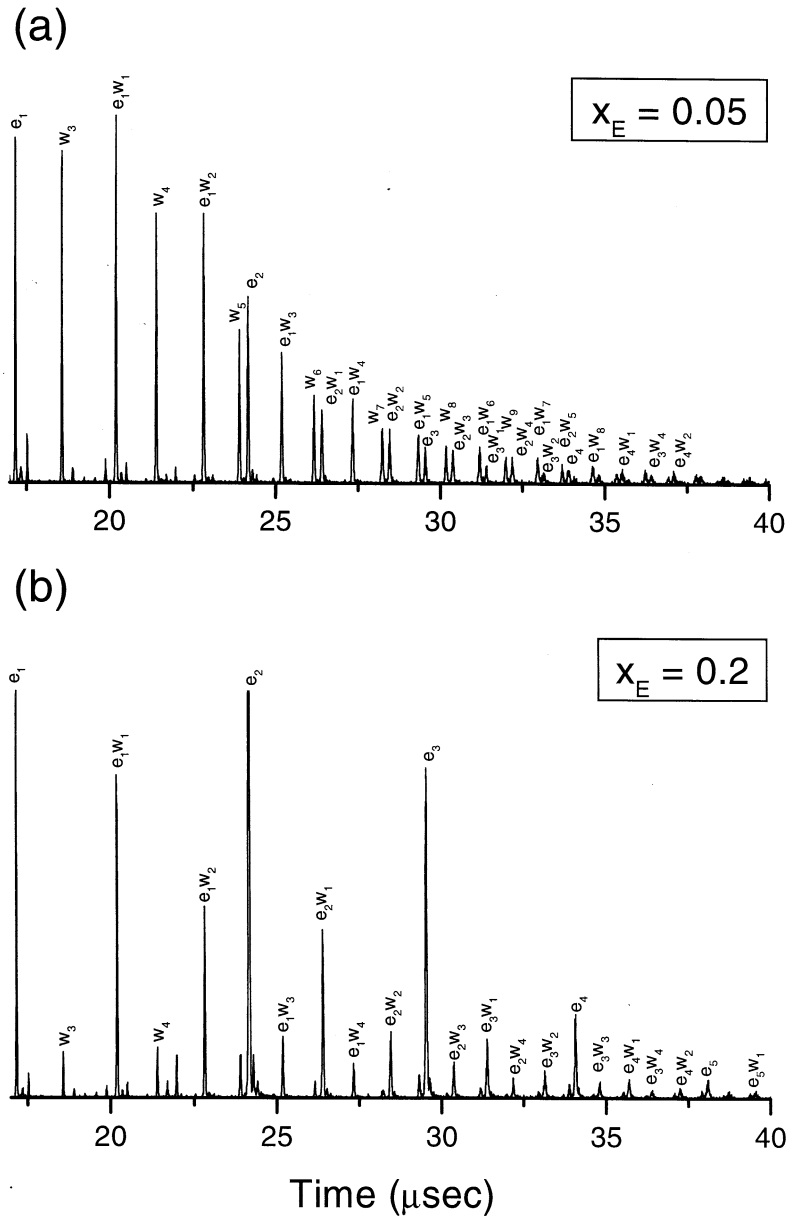

Fig. 2. Time-of-flight mass spectra from ethanol–water mixtures for ethanol mole fraction in the liquid, x_E, of (a) 0.05 and (b) 0.2. The peaks are assigned to various protonated neat clusters of ethanol and water as well as mixed clusters.

3000 and 1800 V, respectively. A microchannel plate detector (RMJ) was used for the detection of the ionized clusters. Mass spectra were collected using a multichannel scalar set to 16,000 channels with a dwell time of 5 ns per channel. For each binary mixture, the spectrum was collected under similar conditions after averaging the data in each channel over 5000 sweeps. Measurements were repeated at a few molar compositions to ascertain the reproducibility in the experiments. To avoid residual contamination from a

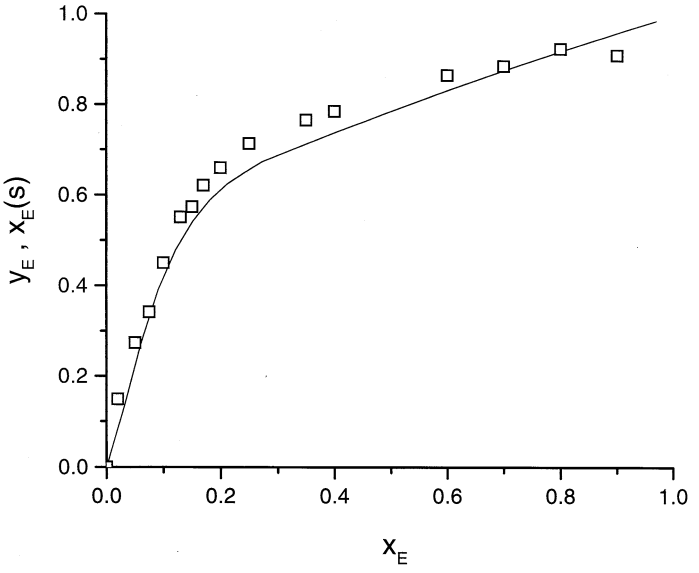

Fig. 3. Variation in the ethanol mole fraction in the vapor, y_E (squares) with the ethanol mole fraction in the liquid, x_E. The solid curve represents the surface mole fraction of ethanol, x_E(s) taken from reference [5].

previous experiment, the pulse valve was pumped out each time before filling in the fresh vapor. A computer code developed in the laboratory has been used to analyze the mass spectra in terms of the abundance and the internal compositions of the various cluster species.

3. Results and Discussion

In Fig. 2, we show the TOF mass spectra obtained with ethanol–water mixtures corresponding to the liquid mole fractions of ethanol, x_E, of 0.05 and 0.2. For $x_E = 0.05$, the mass spectrum exhibits peaks caused by neat ethanol and water clusters (e_nH^+ and w_nH^+) as well as mixed clusters ($e_nw_mH^+$, $1 \leq m \leq 8$). The e_nH^+ clusters become prominent when $x_E \geq 0.2$, as can be seen from Fig. 2b, the next prominent species being $e_nw_1H^+$.

We could obtain the values of the vapor mole fraction of ethanol, y_E, by counting the number of ethanol molecules in the neat as well as the mixed cluster species. In Fig. 3, we show the variation of y_E, with the liquid mole fraction of ethanol, x_E, in the ethanol–water mixtures. We have also plotted the values of the surface mole fraction of ethanol, x_E(s), reported by Laaksonen [5], against x_E in Fig.3 (solid line). It is truly remarkable that the variation of x_E(s) is similar to that of y_E. Clearly, y_E from mass spectrometry directly provides the surface concentration of the ethanol–water mixture.

To compare our results quantitatively with those from surface tension and other measurements [2,4,6], we had to convert the surface excess values expressed as mol cm^{-2} in the literature to x_E(s) values. Thus, in the case of neutron diffraction data [6], the surface layer is taken to be 5.5 Å thick (approximate length of ethanol molecule), and the number of moles per cubic centimeter of ethanol in the surface layer is obtained by adding the surface excess of ethanol per cubic centimeter to the bulk concentration. A similar quantity was obtained for water by subtracting the surface excess from the bulk. These values were used to estimate x_E(s). In Table 1, we list our results along with the values from surface tension for the compositions where neutron results are also available. As can be seen from the table, the surface mole fraction values of ethanol obtained from our experiments agree well with the values obtained previously, especially for dilute solutions ($x_E < 0.1$). At $x_E = 0.1$, the

Table 1
Surface mole fraction of ethanol from different methods

	Based on surface tension				
x_E	Schofield [2] x_E (S)	Guggenheim [4] x_E (S)	Laaksonen [5] x_E (S)	Neutron reflection [6] x_E (S)	Our experiment y_E
0.022	0.17	0.17	0.10	0.12	0.14
0.045	0.25	0.24	0.20	0.21	0.25
0.1	0.35	0.35	0.42	0.34	0.45
0.24	0.59	0.56	0.65	0.62	0.72

surface mole fraction we obtained matches closely that of Laaksonen [5] but is slightly higher compared with the values from other sources [2,4,6]. For x_E = 0.24, the x_E(s) value from our method seems to be slightly larger. It is noteworthy that the mass spectrometric technique employed by us enables the measurement of surface compositions over the entire range of x_E, as shown in Fig. 3. Unlike the neutron diffraction results, mass spectrometry is not model dependent.

4. Conclusion

The mass spectrometric determination of the composition of the binary vapor swept off the surface of ethanol–water mixtures accurately reflects the surface composition of the liquid mixture. The values of the surface concentration obtained by mass spectrometry are in close agreement with those from other measurements based on surface tension and neutron reflection. Unlike the neutron reflection method, which is sensitive to the contrast in scattering of the surface layer and the bulk, the mass spectrometric method can be employed to probe the surface composition over the entire composition range of binary mixtures where the components possess high vapor pressures and have high miscibility.

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