Notes

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A gas chromatographic study of a ternary liquid system

Among the numerous applications of GC, the vast majority are of the analytical type. However, the capabilities of the technique are such that widely different types of physico-chemical studies can also be carried out[1,2]. Among such numerous applications mention may be made of the determination of the activity coefficients of a large number of solutes at infinite dilution in several high-boiling liquids used as stationary phases in GLC columns from measurements of specific retention volumes[3-7]. Although by this method the activity coefficients of hundreds of liquids have been determined, it suffers from the drawback that activity coefficients of solutes can be determined only at infinite dilution and only with the stationary phase in the column as the solvent.

The present study is also concerned with the determination of activity coefficients in liquid systems but by an entirely new technique developed by ARNIKAR *et al.*[8]. They determined the activity coefficients of the components of several binary liquid systems and the results are in good agreement with those obtained by classical methods. The principle is to saturate a quantity of the carrier gas with the vapour over the binary system of known composition and inject a definite volume of it into the column and record the signals for both the components. Similarly, signals are also recorded for the same volume of carrier gas saturated individually with the vapours of the pure liquid at the same temperature. If h is the signal for a component in a solution in which its mole fraction is x and if h_0 is the signal for the vapour of the pure liquid, it has been shown that

$$h/h_0 = \gamma x \tag{1}$$

where γ is its activity coefficient. This method does not have the limitations of the method mentioned earlier; it can be applied to the determination of activity coefficients of the components of any binary system of volatile liquids of any chosen composition. A further advantage of this method is that it can easily be extended to ternary systems. The present work has been undertaken specifically to emphasize this point, since the activity coefficient data for such systems are scarce. Data have been presented for the activity coefficients of the components in the carbon disulphide, *n*-pentane and diethyl ether system over a wide range of compositions.

Experimental

Analytical grade carbon disulphide, *n*-pentane and diethyl ether were used in the present study and several solutions were prepared in which the mole fraction of carbon disulphide was varied between 0.2 and 0.8 and the rest of the composition was made up of various proportions of *n*-pentane and diethyl ether.

The vapour over each solution was analysed by a Beckman gas chromatograph GC-2. The carrier gas was nitrogen at a flow rate of 40 ml/min. The column was a 1.5-m long, 6-mm I.D. tube packed with Celite (40–60 mesh) loaded for 20% with polyethylene glycol (PEG-4000) and maintained at 70°. The detector was a katharometer operating at a filament current of 150 mA. The signals were recorded on a Bristol Dynamaster recorder with a sensitivity of 1 mV for full-scale deflection.

The solution was filled into two glass spirals connected in series, each 150 cm long and 7 mm wide and kept in a thermostat at 24.0°. Nitrogen was bubbled through the solution at a rate of 10 ml/min through fine orifices at the bottoms of the spirals. The gas thus saturated with the vapours of the solution was led through the gas sampling valve of the gas chromatograph. This valve had a matched pair of loops (each of 5 ml volume) and at any time one of the loops was in series with the column while the other was open to the atmosphere. The nitrogen saturated with the vapours of the solution was led into the latter loop. On turning the valve handle through a right angle, the two loops exchanged positions and the vapours enclosed in the loop were led by the carrier gas into the column. The signals for the various components were then recorded. The signals for the saturated vapours of the pure liquids were similarly recorded, by taking them individually in the spirals. The column packing was so chosen that the peaks for the various components were sharp, so that the peak height was proportional to the signal without any appreciable error. The activity coefficient was then calculated in each case by eqn. 1.

TABLE I

ACTIVITY COEFFICIENTS IN TERNARY LIQUID SYSTEM OF CARBON DISULPHIDE, *n*-PENTANE AND DIETHYL ETHER

Temperature: 24°. Peak height in number of divisions of chart paper.

Carbon disulphide			*n-Pentane*			*Diethyl ether*		
Mole fraction	*Peak height*	*Activity coefficient*	*Mole fraction*	*Peak height*	*Activity coefficient*	*Mole fraction*	*Peak height*	*Activity coefficient*
1.00	101	1.00	1.00	91	1.00	1.00	72	1.00
0.80	93	1.15	0.20	39	2.14	0.00	0	—
0.80	92	1.14	0.00	0	—	0.20	30	2.08
0.60	80	1.32	0.40	52	1.43	0.00	0	—
0.60	79	1.30	0.20	31	1.70	0.20	28	1.95
0.60	78	1.29	0.00	0	—	0.40	44	1.53
0.40	64	1.58	0.60	69	1.26	0.00	0	—
0.40	62	1.54	0.40	52	1.43	0.20	27	1.88
0.40	62	1.54	0.20	32	1.76	0.40	45	1.56
0.40	61	1.51	0.00	0	—	0.60	55	1.27
0.20	39	1.93	0.80	79	1.09	0.00	0	—
0.20	38	1.88	0.60	66	1.21	0.20	26	1.81
0.20	37	1.83	0.40	52	1.43	0.40	45	1.56
0.20	36	1.78	0.20	30	1.65	0.60	55	1.27
0.20	36	1.78	0.00	0	—	0.80	65	1.13

Table I presents data for the activity coefficient of all the three components at various compositions of the solution.

Results and discussion

The data in Table I show that the activity coefficients of the various components in the ternary system can be determined over wide ranges of concentrations of each component by this new GC technique. The method is simple and can easily be adopted for the study of any multicomponent system of volatile liquids.

For obtaining accurate results, it is necessary to evaluate the signals precisely. This can readily be done by measuring the peak heights when the peaks are narrow and sharp as in the present case. In other cases, one has to resort to more accurate methods for correlating the peaks with the signal strength such as by using disc integrators for measuring peak areas. By such means the utility of the method under present discussion can be improved.

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