

Simultaneous Measurements of Heat Capacities and Densities of Organic Liquid Mixtures—Systems Containing Ketones

Jean-Pierre E. Grolier¹ and George C. Benson²

Division of Chemistry, National Research Council of Canada, Ottawa, Ont., Canada K1A 0R6

Patrick Picker

Département de Chimie, Université de Sherbrooke, Sherbrooke, Que., Canada J1K 2R1

Flow techniques were used to determine the relative volumetric specific heat and the density on the same sample at 298.15K for each of the solvents: benzene, carbon tetrachloride, 2-butanone, and 2-pentanone. Similar measurements were also carried out on binary mixtures of each of the ketones with benzene and with carbon tetrachloride. Excess heat capacities and excess volumes were calculated from the results.

Determination of excess heat capacities and excess volumes for binary mixtures of the ketones 2-butanone and 2-pentanone with benzene and with carbon tetrachloride was undertaken to supplement measurements of excess enthalpies in progress for the same systems. Adoption of flow techniques made it possible to measure both the heat capacity and density on the same sample of liquid.

Experimental

The flow calorimeter and densimeter used for the present measurements were built by Picker et al. (9–11) at the Université de Sherbrooke and have been used previously for studying aqueous solutions (1–4, 6–8). Reference can be made to these earlier publications for details of the apparatus and operating procedures. The following paragraphs give only brief descriptions of the main features of the instruments and some changes in operating technique necessitated by their application to organic liquid mixtures.

Calorimetric measurements. The flow microcalorimeter for heat capacities (10) is essentially a differential thermal balance which measures directly the ratio of the volumetric specific heat of a liquid flowing through the working cell relative to that of a liquid flowing through the reference cell. (Volumetric specific heat = heat capacity per unit volume = C_p/V .) The two cells are of identical construction; each has a heater (Zener diode junction) and a thermal detector (thermistor). Before entering the cells, the liquids are brought to the same constant temperature (within 0.5mK) in a thermostat. While passing through the cells, the liquids are heated so that equal temperature increases of about 1.6K are established. Once a steady state has been obtained with a reference liquid of known volumetric specific heat flowing through both cells, the power W dissipated in the working cell is determined from measurements of the Zener current and potential difference, and the liquid to be measured is introduced into the working cell. The calorimeter has a low response time of about 2 sec, and while the new liquid is flowing through the working cell and the reference liquid is still flowing through the second cell, the difference be-

tween the volumetric specific heats of the liquids alters the thermal balance.

A thermal feedback circuit connected to the heaters and controlled by a bridge containing the detectors in adjacent arms changes the power supplied to the working cell by ΔW to keep the gradients of temperature equal in the two cells. Connection of the cells in series ensures that the flow rates are equal and that any fluctuations of flow are identical in the two cells. Under these conditions the thermal feedback makes ΔW independent of the value of the flow rate. At the steady state, ΔW is also independent of the heat capacities of the cells themselves, and the volumetric specific heat of the liquid under investigation is then related to that of the reference liquid by the equation

$$C_p/V = (C_p/V)_0 (1 + \Delta W/W) \quad (1)$$

In the case of aqueous electrolyte solutions, the small differences of volumetric specific heat between the solutions and water used as a reference liquid can be measured with good precision (1–4, 6–8). However, in mixtures of nonelectrolytes, much larger differences of volumetric specific heat may occur, and the use of one component as a reference liquid over the whole concentration range becomes inappropriate if the calorimeter must be operated at a reduced sensitivity.

In our work, measurements on a series of mixtures were made in the order of increasing concentration of one of the components. Starting from zero mole fraction, each mixture was used as a reference liquid for the next in the series. This technique restricted the determinations of volumetric specific heat to small differences which could be measured at full sensitivity (i.e., about $7 \times 10^{-5} \text{ J K}^{-1} \text{ cm}^{-3}$). Checks with different series of mixtures showed that the stepwise procedure did not contribute significantly to the error of the final results. Benzene was used as the ultimate reference liquid, and a value of $136.1 \text{ J mol}^{-1} \text{ K}^{-1}$ (12) was adopted for its heat capacity at 298.15K.

The liquids flowed through the calorimeter and densimeter by gravity at a rate of about $0.0083 \text{ cm}^3 \text{ sec}^{-1}$. Approximately 2–3 cm^3 of liquid were required for a single determination of volumetric specific heat over a time of 4–5 min. The change of power dissipated in the working cell was monitored continuously, and the value of ΔW was determined from the recorder trace. The precision of this determination is estimated to be about 0.3%, and under the best conditions its reproducibility was $\pm 0.2\%$.

Density measurements. The molar volumes of the liquids are needed to calculate heat capacities from Equation 1. Densities were measured with a vibrating tube densimeter (11) which was connected to the outlet of the calorimeter so that the liquid flowed through the two instruments in series. Upon entering the densimeter, the liquid is brought to within 0.5mK of a known constant temperature and then flows through a U-shaped stain-

¹ Visiting French scientist 1972–73 attached to CNRS Paris from the Université de Clermont-Ferrand, Clermont-Ferrand, France.

² To whom correspondence should be addressed.

less-steel tube (o.d. 1.09 mm, i.d. 0.76 mm). The natural vibration period of the tube depends on the density of the liquid and is measured with a high-resolution digital frequency meter.

In the present work, the equation

$$\Delta\rho = \rho - \rho_0 = B(\tau^2 - \tau_0^2) \quad (2)$$

was used to relate the density ρ and period τ for the liquid to corresponding values for the reference liquid. The mean value of the constant B determined previously with aqueous NaCl solutions at 298.15K is $(1.8293 \pm 0.0001) \times 10^{-6} \text{ g cm}^{-3} \text{ sec}^{-2}$ (17).

Values of the densities of the organic solvents and their mixtures were based on the value $0.997047 \text{ g cm}^{-3}$ (5) for the density of water at 298.15K. The reproducibility of the results was about 3 ppm.

Materials. Carbon tetrachloride (GC-spectrophotometric quality from J. T. Baker Chemical Co.) was used without further treatment. Benzene and 2-butanone (MEK) (both certified reagents from Fisher Scientific Co.) and 2-pentanone (MPK) (pure grade from Eastman Organic Chemicals) were purified chromatographically using a column (1.8 m long, 1.9 cm i.d.) packed with Chromosorb P containing 25% Apiezon L. Chromatographic analyses showed that the purities of all of the samples used for the measurements exceeded 99.9 mol %. Densities and heat capacities of the pure components are listed in Table I along with values from the literature (12, 13).

Binary mixtures were prepared by weight in small vials with Teflon septa. The two components were injected into the vial with hypodermic syringes. Each mixture weighed about 10 grams and nearly filled the vial so that vaporization corrections were negligible. The error of the mole fraction is estimated to be less than 0.0001.

Results

The following systems were investigated: MEK+C₆H₆, MEK+CCl₄, MPK+C₆H₆, and MPK+CCl₄. All measurements were made at an average temperature of 298.15K. Table II contains the experimental values of $\Delta W/W$ and $\Delta\rho$ for mixtures with mole fraction x_1 of the ketone component. Benzene was used as the initial reference liquid for the system MEK+C₆H₆. Each mixture in the set then served as reference for the one immediately following it until pure MEK was reached. Starting with MEK as the initial reference liquid for the system MEK+CCl₄, a similar stepwise procedure was continued to pure CCl₄. The two remaining systems were treated in the same manner. Heat capacities and densities derived from the primary experimental results were used to calculate molar excess heat capacities

$$C_p^E = C_p - x_1 C_{p1} - x_2 C_{p2} \quad (3)$$

and molar excess volumes

$$V^E = V - x_1 V_1 - x_2 V_2 \quad (4)$$

These values are also listed in Table II.

The method of least squares was used to fit the results for each of the excess functions with an equation of the form

$$\chi^E = x_1 x_2 \sum_{j=1}^n a_j (x_2 - x_1)^{j-1} \quad (5)$$

containing n adjustable coefficients. The minimum number of these needed to represent each set of results adequately was determined from the changes in the standard error of estimate σ , calculated from

$$\sigma^2 = \sum (\chi^E(\text{Experimental}) - \chi^E(\text{Equation 5}))^2 / (m - n) \quad (6)$$

Table I. Physical Constants of Component Liquids at 298.15K

Component	Density, ρ , g cm ⁻³		Heat capacity, C_p , J mol ⁻¹ K ⁻¹	
	Measd	Lit ^a	Measd	Lit ^b
Benzene	0.87370	0.87368	...	136.1
Carbon tetrachloride	1.58521	1.58437	131.9	133.0
2-Butanone	0.79985	0.79971	159.2	158.9
2-Pentanone	0.80163	0.80147	185.1	...

^a Interpolated from data in ref. 13. ^b Ref. 12.

Table II. Experimental Results for $\Delta W/W$ and $\Delta\rho$ at 298.15K and Corresponding Values of Molar Excess Heat Capacity and Molar Excess Volume

x_1	$10^3 \times \Delta W/W$	$10^3 \times \Delta\rho$, g cm ⁻³	C_p^E , J mol ⁻¹ K ⁻¹	V^E , cm ³ mol ⁻¹
MEK(1)+C ₆ H ₆ (2)				
0.1119	19.49	-8.021	0.149	-0.0314
0.2041	18.33	-6.595	0.630	-0.0580
0.3115	17.67	-7.688	0.730	-0.0876
0.4415	25.24	-9.416	1.485	-0.1104
0.4923	8.77	-3.715	1.663	-0.1151
0.6176	21.84	-9.260	2.185	-0.1149
0.8130	32.23	-14.774	2.916	-0.0735
1.0000	6.51	-14.382	0.0	0.0
MEK(1)+CCl ₄ (2)				
0.9201	-8.10	67.872	1.720	-0.0773
0.8973	-3.10	19.280	2.078	-0.1036
0.8932	-0.99	3.514	2.064	-0.1137
0.8030	-11.13	75.319	3.717	-0.1821
0.6998	-16.00	84.687	5.143	-0.2273
0.5990	-19.69	81.210	5.947	-0.2442
0.5048	-22.62	74.442	6.108	-0.2302
0.4041	-28.36	78.162	5.701	-0.1964
0.3176	-26.94	65.978	5.041	-0.1531
0.2053	-39.83	84.117	3.553	-0.0820
0.1037	-39.20	75.169	1.850	-0.0392
0.0	-41.77	75.610	0.0	0.0
MPK(1)+C ₆ H ₆ (2)				
0.0863	13.00	-7.177	-0.086	-0.0178
0.2023	17.11	-9.201	-0.138	-0.0495
0.3104	15.40	-8.238	-0.125	-0.0765
0.4071	12.63	-7.115	-0.174	-0.0979
0.5052	12.37	-7.021	-0.187	-0.1128
0.6159	13.16	-7.774	-0.192	-0.1119
0.6996	9.41	-5.746	-0.194	-0.1025
0.8214	13.29	-8.169	-0.136	-0.0751
0.9151	9.56	-6.152	-0.096	-0.0407
0.9378	2.33	-1.468	-0.069	-0.0314
1.0000	6.21	-4.007	0.0	0.0
MPK(1)+CCl ₄ (2)				
0.9124	-7.78	63.294	1.499	-0.0953
0.9024	-1.15	7.291	1.628	-0.1049
0.8385	-7.09	46.819	2.536	-0.1499
0.7954	-5.35	31.812	3.086	-0.1665
0.6590	-20.54	102.478	4.282	-0.2112
0.5005	-31.22	122.169	4.729	-0.2101
0.4344	-15.86	51.852	4.608	-0.1872
0.2996	-37.37	107.596	3.790	-0.1191
0.1912	-35.15	88.502	2.670	-0.0554
0.1129	-28.34	65.351	1.619	-0.0245
0.0534	-22.89	50.441	0.756	-0.0060
0.0318	-8.64	18.448	0.436	0.0018
0.0	-12.50	27.527	0.0	0.0

Table III. Values of Coefficients a_j in Equation 5 Determined by Method of Least Squares

System	Function, X^E	a_1	a_2	a_3	a_4	σ
MEK+C ₆ H ₆	$C_p^E, \text{J mol}^{-1} \text{K}^{-1}$	6.755	-12.228	10.133		0.185
	$V^E, \text{cm}^3 \text{mol}^{-1}$	-0.4637	0.1077	0.1146		0.0007
MEK+CCl ₄	$C_p^E, \text{J mol}^{-1} \text{K}^{-1}$	24.458	-1.708	-5.118		0.055
	$V^E, \text{cm}^3 \text{mol}^{-1}$	-0.9221	0.5026	0.2676		0.0045
MPK+C ₆ H ₆	$C_p^E, \text{J mol}^{-1} \text{K}^{-1}$	-0.723	0.178	-0.478		0.016
	$V^E, \text{cm}^3 \text{mol}^{-1}$	-0.4412	0.1727	0.0976		0.0012
MPK+CCl ₄	$C_p^E, \text{J mol}^{-1} \text{K}^{-1}$	18.946	-0.946	-2.531	-1.176	0.016
	$V^E, \text{cm}^3 \text{mol}^{-1}$	-0.8208	0.4578	0.2443	0.2447	0.0040

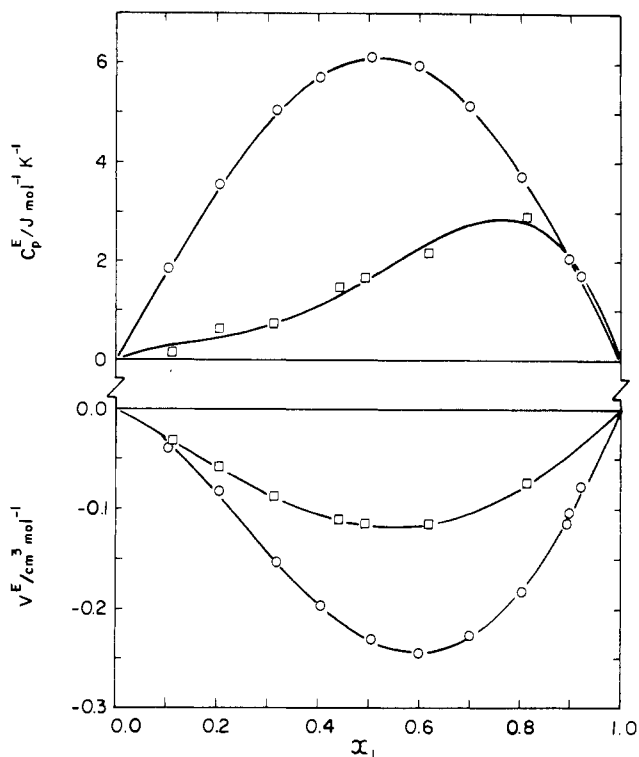


Figure 1. Molar excess heat capacities and molar excess volumes of 2-butanone systems at 298.15K. Experimental results: \square , MEK(1)+C₆H₆(2); \circ , MEK(1)+CCl₄(2). Curves are smoothed representations by Equation 5

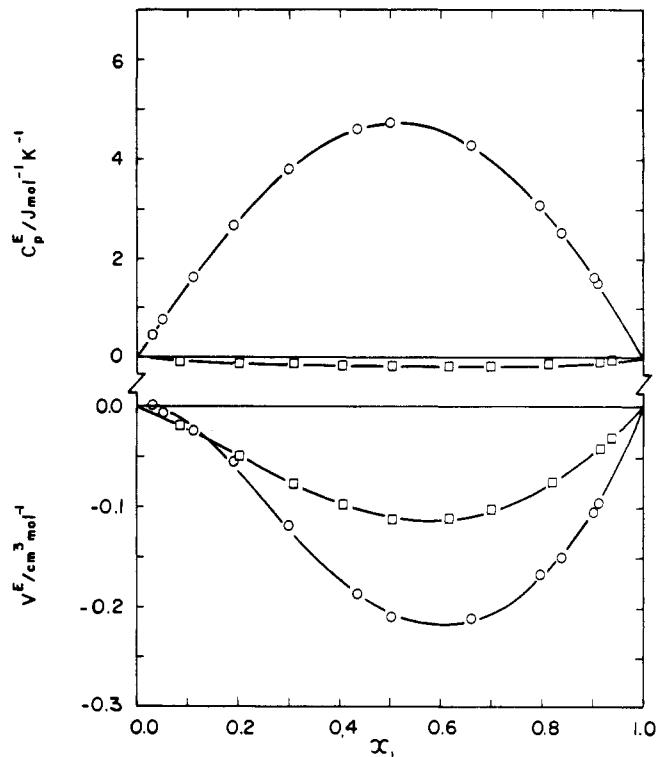


Figure 2. Molar excess heat capacities and molar excess volumes of 2-pentanone systems at 298.15K. Experimental results: \square , MPK(1)+C₆H₆(2); \circ , MPK(1)+CCl₄(2). Curves are smoothed representations by Equation 5

for successively larger values of n . The summation in Equation 6 is taken over the m values in a set of experimental results. Values of the coefficients obtained from this analysis are given in Table III along with the standard error of estimate associated with each representation. Plots of the experimental results and their least-squares representations are shown in Figures 1 and 2.

The excess volume curves are negative for all of the systems and tend to be skewed toward mixtures rich in ketone. This could be due to dipole-induced dipole interaction between the dipole of the ketone and the polarizable molecules of benzene and carbon tetrachloride. The excess heat capacity curves are all positive except for the mixtures of MPK+C₆H₆ which have small negative values nearly equal to zero for the whole concentration range.

The present work illustrates the feasibility of using flow techniques for simultaneous determinations of the specific heat and density of mixtures of nonelectrolytes. The measurements can be made in a short time with good accuracy and require relatively small quantities of the components.

Acknowledgment

We are indebted to J.-L. Fortier for helpful discussions. We also thank C. J. Halpin and P. J. D'Arcy for technical assistance.

Nomenclature

- $a_1, a_2 \dots a_j$ = coefficients in representations of excess properties by Equation 5
- B = calibration constant in Equation 2, $\text{g cm}^{-3} \text{sec}^{-2}$
- C_p = molar heat capacity, $\text{J mol}^{-1} \text{K}^{-1}$
- C_p^E = molar excess heat capacity, $\text{J mol}^{-1} \text{K}^{-1}$
- n = number of coefficients in Equation 5
- m = number of experimental results
- V = molar volume of pure component or mixture, $\text{cm}^3 \text{mol}^{-1}$
- V^E = molar excess volume, $\text{cm}^3 \text{mol}^{-1}$
- W = power, J sec^{-1}
- X^E = typical molar excess property
- x_i = mole fraction of component i

Greek Letters

ρ = density g cm⁻³

σ = standard error of estimate defined by Equation 6

τ = vibration period, sec

Subscripts

0 = reference liquid (pure component or mixture)

1 = ketone component in mixture

2 = nonpolar component in mixture (benzene or carbon tetrachloride)

Literature Cited

- (1) Desnoyers, J. E., Pagé, R., Perron, G., Fortier, J.-L., Leduc, P.-A., Platford, R. F., *Can. J. Chem.*, **51**, 2129 (1973).
- (2) Desrosiers, N., Perron, G., Mathieson, J. G., Conway, B. E., Desnoyers, J. E., *J. Solution Chem.*, **3**, 789 (1974).

- (3) Fortier, J.-L., Leduc, P.-A., Desnoyers, J. E., *Ibid.*, **3**, 323 (1974).
- (4) Fortier, J.-L., Philip, P. R., Desnoyers, J. E., *ibid.*, p 523.
- (5) Kell, G. S., *J. Chem. Eng. Data*, **12**, 66 (1967).
- (6) Leduc, P.-A., Desnoyers, J. E., *Can. J. Chem.*, **51**, 2993 (1973).
- (7) Leduc, P.-A., Fortier, J.-L., Desnoyers, J. E., *J. Phys. Chem.*, **78**, 1217 (1974).
- (8) Philip, P. R., Desnoyers, J. E., Hade, A., *Can. J. Chem.*, **51**, 187 (1973).
- (9) Picker, P., *Can. Res. Develop.*, **7** (1), 11 (1974).
- (10) Picker, P., Leduc, P.-A., Philip, P. R., Desnoyers, J. E., *J. Chem. Thermodyn.*, **3**, 631 (1971).
- (11) Picker, P., Tremblay, E., Jolicoeur, C., *J. Solution Chem.*, **3**, 377 (1974).
- (12) Riddick, J. A., Bunger, W. B., "Organic Solvents," 3rd ed., Vol II, "Techniques of Chemistry," A. Weissberger, Ed., Wiley-Interscience, New York, N.Y., 1970.
- (13) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds. Vol I and II," Elsevier, New York, N.Y., 1950, 1965.

Received for review October 14, 1974. Accepted February 8, 1975. Issued as NRCC No. 14648.

Solubility Product of Thallium(I) Thiocyanate in Water at 10–40°C

Wojciech J. Popiel¹ and Eid Hashem Tamimi

Chemistry Department, University of Jordan, Amman, Jordan

With an ion-selective electrode the thiocyanate activities in saturated aqueous solutions of thallium(I) thiocyanate were measured at seven temperatures in the range 10–40°C, and the solubility products were calculated. The logarithm of the solubility product is a linear function of the reciprocal of the absolute temperature, and the heat of solution of the compound is 66.25 kJ mol⁻¹.

The solubility product (K) of TISCN was determined potentiometrically by Suzuki (6), who reported a value of 1.7×10^{-4} at 25°C, whereas a subsequent similar study by Golub and Skorobogatko (2) gave 1.35×10^{-4} at 20°C and 7.91×10^{-4} at 40°C. From polarographic measurements, Sundaram et al. (5) obtained a value of 2.31×10^{-4} at 30°C. The above results appear to lack consistency since a plot of $\log K$ against the reciprocal of the absolute temperature does not yield the expected straight line.

The recent development of the thiocyanate ion-selective electrode presents a new and relatively simple method of measuring ionic activity directly, and from it the activity solubility product. One possible source of error thereby avoided is the effect of incomplete dissociation of thallium(I) thiocyanate. In addition to the ion-pair TISCN, ionic complexes of the type $Tl(SCN)_n^{(1-n)}$ are known to form at higher concentrations of the thiocyanate ion. However, several studies indicate that such complexing is weak (1, 2, 4), and no allowance for it has been made in the present work.

Experimental

Thallium(I) thiocyanate was prepared by precipitation from equimolar solutions of thallium(I) sulfate and sodium thiocyanate. After filtration the product was washed and recrystallized several times from hot water.

Saturated solutions of thallium(I) thiocyanate were prepared by adding a slight excess of the salt to a convenient

¹ Present address, Chemistry Department, Makerere University, P.O. Box 7062, Kampala, Uganda. To whom correspondence should be addressed.

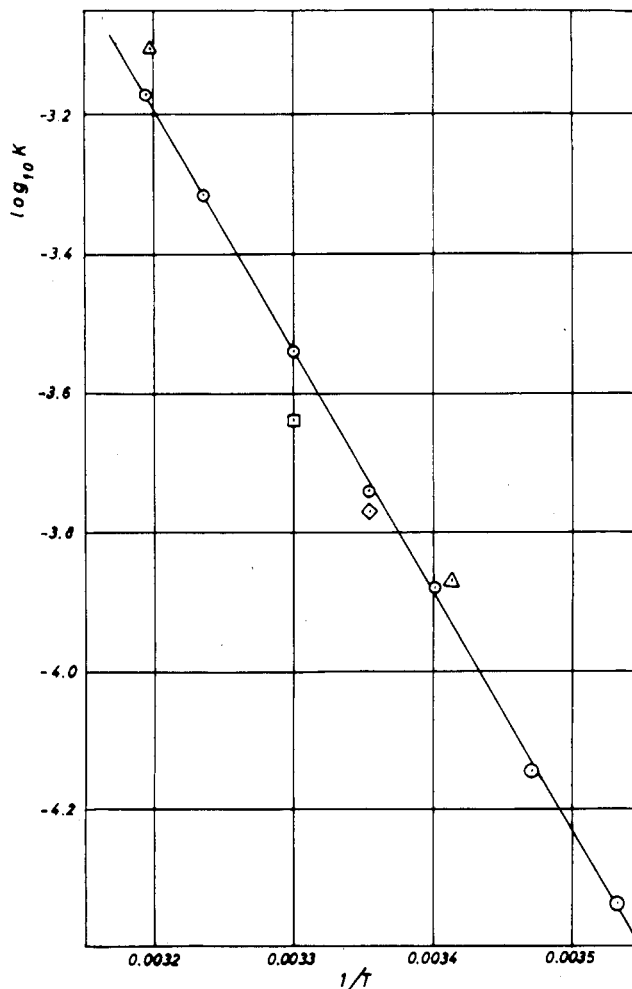


Figure 1. Least-squares plot of logarithm of solubility product (K) of thallium(I) thiocyanate against reciprocal of absolute temperature (7). Experimental points: \odot , present work; Δ , Golub and Skorobogatko (2); \square , Sundaram and coworkers (5); \diamond , Suzuki (6)