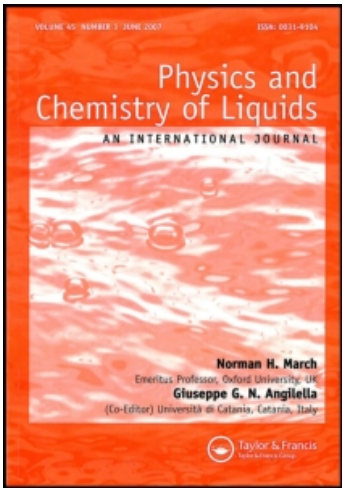

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Some Physical Properties of Binary Liquid Systems: (2-Butanone *n*-Propionic Acid or *n*-Butyric Acid)

R. K. Wanchoo[a]; J. Narayan[a]
[a] Department of Chemical Engineering and Technology, Panjab University, Chandigarh, India

To cite this Article Wanchoo, R. K. and Narayan, J.(1994) 'Some Physical Properties of Binary Liquid Systems: (2-Butanone *n*-Propionic Acid or *n*-Butyric Acid)', Physics and Chemistry of Liquids, 27: 3, 159 — 167
To link to this Article: DOI: 10.1080/00319109408029521
URL: http://dx.doi.org/10.1080/00319109408029521

Phys. Chem. Liq., 1994, Vol. 27, pp. 159–167
Reprints available directly from the publisher
Photocopying permitted by license only

SOME PHYSICAL PROPERTIES OF BINARY LIQUID SYSTEMS: (2-BUTANONE + *n*-PROPIONIC ACID OR *n*-BUTYRIC ACID)

R. K. WANCHOO* and J. NARAYAN

Department of Chemical Engineering and Technology
Panjab University, Chandigarh-160 014, India

(Received 7 April 1993)

Density, viscosity and surface tension of two binary liquid systems: 2-butanone + *n*-propionic acid, 2-butanone + *n*-butyric acid have been determined at 20, 30 and 40°C, over the whole compositional range. The excess values of molar volume, viscosity, Gibbs free energy for the activation of flow and surface tension were evaluated. These excess values were fitted to a Redlich–Kister type of equation. The Grunberg–Nissan parameter, *d*, was also calculated. The binary viscosity data were fitted to the models of McAllister, Heric, Auslander and Teja and Rice. Surface tension data were fitted to the models of Zihao and Jufu, Rice and Teja, and an empirical two-constant model proposed in this study.

KEY WORDS: Excess molar volume, viscosity, activation energy, surface tension.

INTRODUCTION

As an extension to our previous work[1–4] on the measurement of transport and surface properties of non-electrolyte mixtures, in the present study densities, viscosities and surface tensions of the binary organic liquid mixtures of 2-butanone with *n*-propionic acid or *n*-butyric acid have been found experimentally at 20, 30 and 40°C. From these experimental results, excess properties have been determined and studied in terms of sign and magnitude of the physical properties in the respective mixtures. Valuable information about the presence of secondary bonding forces in a particular system is derived from the study. Also, the entire data on excess properties have been fitted to the Redlich-Kister type of equation. The mixture viscosity data have been fitted to the models of McAllister, Heric, Auslander and Teja and Rice. Binary surface tension data have been fitted to the models of: Zihao and Jufu, Rice and Teja and an empirical two-parameter model.

EXPERIMENTAL SECTION

2-butanone, *n*-propionic acid and *n*-butyric acid (S.D's grade) were purified by

* Author to whom correspondence should be addressed.
† Dept. of Chemical Engg., REC, Srinagar.

Table 1 Physical Constants of Pure Components at 20°C

Property	*2-Butanone*		*n-Propionic acid*		*n-Butyric acid*	
	Lit.[5]	*Sample used*	*Lit.*[5]	*Sample used*	*Lit.*[5]	*Sample used*
Density (g/cm^3)	0.8049	0.8050	0.9934	0.9930	0.9582	0.9580

the standard procedures[5]. The purity of all the components was checked by comparing their experimental density with that of literature values[5]. For each run, a fresh liquid mixture was prepared on mass basis, using a Mettler balance (precision of 1×10^{-5} g). The purity of each component with respect to the corresponding literature values is recorded in Table 1.

Densities of the pure components and their mixtures were measured with a thoroughly cleaned pyknometer calibrated at 20, 30 and 40°C with mercury[6]. At each temperature, the densities were determined with a precision of about ± 0.01 percent.

Viscosities were determined with the help of a modified Ubbelohode viscometer[7]. At each temperature the viscometer was calibrated against the known viscosities of benzene and carbon tetrachloride[6]. The constants of the viscometer at each temperature were determined from the following equation:

$$\nu = \eta/\rho = at - b/t \tag{1}$$

where, a and b are the temperature dependent constants of the viscometer. At a particular temperature, an average value of the efflux time (t) of the mixture and corresponding values of a and b were used in Eq. (1) for the calculation of kinematic viscosity (ν). Using the density values of the respective mixtures, the absolute viscosity (η) was thus calculated. The accuracy of the viscosity measurements is of the order of 0.001 cP.

Similarly, surface tension of the pure components and that of their mixtures was determined by the differential capillary rise method[6]. The difference (ΔH), in the level of liquid in two capillaries was measured with a cathetometer reading to 0.05 mm. An average reproducibility of better than 0.01 mm was obtained. The difference in the levels of liquid in two capillaries of different radii is related to the surface tension of the liquid by the relation:

$$h_1 - h_2 = \Delta H = (2\sigma/\rho g)A + B - C \tag{2}$$

The constants A, B and C were calculated using the standard values of surface tension of benzene and ethylacetate at 20°C. For each mixture of the respective systems, ΔH was recorded at three different temperatures over the entire compositional range. The surface tension of each mixture was thus calculated from Eq. (2).

The entire experimental data for both the systems is recorded in Table 2. All the

Table 2 Mole fraction (x_1), density (ρ), viscosity (η), surface tension (σ) and Grunberg–Nissan parameter (d) for various systems.

x_1	ρ (g/cm^3)	η (cP)	σ ($dyne/cm$)	d
System 2-Butanone + *n*-Propionic acid, 20°C				
0.0000	0.993000	1.102200	26.70	—
0.847	0.978160	1.037500	26.66	0.2532
0.1723	0.962600	0.972200	26.59	0.2628
0.2585	0.947170	0.909300	26.49	0.2720
0.3570	0.929100	0.839300	26.35	0.2841
0.4544	0.911040	0.771800	26.17	0.2965
0.5554	0.892040	0.703800	25.95	0.3110
0.6602	0.872020	0.635400	25.68	0.3285
0.7691	0.850900	0.566500	25.36	0.3488
0.8822	0.828600	0.497400	24.97	0.3737
1.0000	0.805000	0.428000	24.52	—
System 2-Butanone + *n*-Propionic acid, 30°C				
0.0000	0.983000	0.958000	25.71	—
0.0847	0.966160	0.902200	25.60	0.2120
0.1723	0.950600	0.846000	25.47	0.2186
0.2585	0.936170	0.792100	25.33	0.2251
0.3570	0.917100	0.732400	25.14	0.2339
0.4544	0.899040	0.675100	24.94	0.2426
0.5554	0.880040	0.617700	24.69	0.2528
0.6602	0.860020	0.556000	24.44	0.2308
0.7691	0.838900	0.502700	24.13	0.2776
0.8822	0.816600	0.445500	23.85	0.2943
1.0000	0.793950	0.388500	23.40	—
System 2-Butanone + *n*-Propionic acid, 40°C				
0.0000	0.973000	0.845100	24.72	—
0.0847	0.954160	0.797500	24.40	0.2184
0.1723	0.938670	0.749400	24.12	0.2258
0.2585	0.924170	0.703100	23.86	0.2330
0.3570	0.905100	0.651600	23.53	0.2427
0.4544	0.887050	0.601900	23.21	0.2521
0.5554	0.868040	0.551900	23.06	0.2636
0.6602	0.848020	0.501500	22.89	0.2765
0.7691	0.826900	0.450800	22.69	0.2914
0.8822	0.804600	0.400000	22.51	0.3100
1.0000	0.783000	0.349000	22.28	—
System 2-Butanone + *n*-Butyric acid, 20°C				
0.0000	0.958000	1.540200	26.74	—
0.1024	0.945920	1.382700	26.65	0.2530
0.2043	0.933090	1.235900	26.49	0.2553
0.3057	0.919540	1.099600	26.31	0.2568
0.4065	0.905270	0.973700	26.11	0.2569
0.5067	0.890320	0.858200	25.89	0.2561
0.6064	0.874670	0.752600	25.65	0.2530
0.7056	0.858340	0.656900	25.39	0.2475
0.8043	0.841330	0.571000	25.12	0.2393
0.9024	0.823690	0.494800	24.83	0.2276
1.0000	0.805000	0.428000	24.52	—

Table 2 (*continued*)

x_1	ρ (g/cm^3)	η (cP)	σ	d
System 2-Butanone + *n*-Butyric acid, 30°C				
0.0000	0.948000	1.330400	25.57	—
0.1024	0.935530	1.200200	25.41	0.2509
0.2043	0.922090	1.078300	25.06	0.2546
0.3057	0.908130	0.964600	24.74	0.2581
0.4065	0.893540	0.858900	24.46	0.2603
0.5067	0.878310	0.761000	24.21	0.2605
0.6064	0.862460	0.671600	23.98	0.2634
0.7056	0.845990	0.589700	23.79	0.2644
0.8043	0.828910	0.515000	23.63	0.2603
0.9024	0.811240	0.448500	23.50	0.2665
1.0000	0.793050	0.388500	23.40	—
System 2-Butanone + *n*-Butyric acid, 40°C				
0.0000	0.938040	1.120500	24.72	—
0.1024	0.924680	1.020800	24.37	0.2857
0.2043	0.910810	0.926300	23.99	0.2951
0.3057	0.896420	0.836800	23.66	0.3046
0.4065	0.881610	0.752500	23.36	0.3152
0.5067	0.866320	0.673300	23.09	0.3269
0.6064	0.850550	0.598900	22.86	0.3390
0.7056	0.834320	0.529300	22.67	0.3518
0.8043	0.817640	0.464500	22.51	0.3660
0.9024	0.800540	0.404400	22.38	0.3802
1.0000	0.783000	0.349000	22.28	—

measurements were made at a constant temperature with the help of a circulating type ultra cryostat (type MK 70, MLW, Germany) to within ± 0.02 K.

The Grunberg–Nissan parameter[8], d, was determined using the following expression:

$$d = \left[\frac{\ln \eta_{mix} - x_1 \ln \eta_1 - x_2 \ln \eta_2}{x_1 x_2}\right] \tag{3}$$

From the experimental data, excess properties viz; V^E, η^E, G^E and σ^E were calculated using the following expressions[9]:

$$V^E = x_1 M_1[\rho_{mix}^{-1} - \rho_1^{-1}] + x_2 M_2[\rho_{mix}^{-1} - \rho_2^{-1}] \tag{4}$$

$$\log(1/\eta^0) = x_1 \log(1/\eta_1) + x_2 \log(1/\eta_2)$$

$$\eta^E = \eta_{mix} - \eta^0 \tag{5}$$

$$G^E/RT = [\ln \eta_{mix} V_{mix} - \{x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2\}] \tag{6}$$

$$\sigma^E = \sigma_{mix} - [x_1\sigma_1 + x_2\sigma_2] \tag{7}$$

The values of V^E, η^E, G^E and σ^E were fitted with a Ridlich–Kister type of Eq.[10], using least squares method.

$$P^E = x_1 x_2 \sum_{1}^{n} A_{j-1}(2x_1 - 1)^{j-1} \tag{8}$$

where P^E represents the excess property, A_j is the polynomial coefficient and n the polynomial degree. The results thus obtained are recorded in Table 3.

The following theoretical models for mixture viscosities have been tested with the experimental data. McAllister's[11] equation derived on the basis of Eyring's absolute reaction rate theory is:

$$\begin{aligned}\ln \eta_{mix} = {} & x_1^3 \ln \eta_1 + x_2^3 \ln \eta_2 + 3x_1^2 x_2 \ln \eta_{12} + 3x_1 x_2^2 \ln \eta_{21} \\ & - \ln[x_1 + x_2(M_2/M_1)] + 3x_1^2 x_2 \ln[\tfrac{2}{3} + (M_2/3M_1)] \\ & + 3x_1 x_2^2 \ln[\tfrac{1}{3} + 2M_2/3M_1] + x_2^3 \ln[M_2/M_1],\end{aligned} \tag{9}$$

where η_{12} and η_{21} are the interaction parameters. Heric's[12] equation has the following form:

$$\ln \eta_{mix} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 \ln M_1 + x_2 \ln M_2 - \ln(x_1 M_1 + x_2 M_2) + \delta_{12} \tag{10}$$

where δ_{12} is a deviation function expressed as:

$$\delta_{12} = x_1 x_2[\beta_{12} + \beta_{21}(x_1 - x_2)] \tag{11}$$

Auslander's[13] model is represented by:

$$x_1(x_1 + B_{12}x_2)(\eta_{mix} - \eta_1) + A_{21}x_2(B_{21}x_1 + x_2)(\eta_{mix} - \eta_2) = 0 \tag{12}$$

where B_{12}, A_{21} and B_{21} are parameters representing binary interactions.
For a binary mixture, the Teja and Rice[14] equation based on theory of corresponding states can be written as:

$$\ln(\eta_{mix}\varepsilon_{mix}) = x_1 \ln(\eta_1 \varepsilon_1) + x_2 \ln(\eta_2 \varepsilon_2) \tag{13}$$

where,

$$\varepsilon_i = V_{ci}^{2/3}/(T_{ci}M_i)^{1/2} \qquad \text{for } i = 1, 2 \text{ or mix}$$

Table 3 Coefficients of Eq. (8) and standard deviations (SD) determined by the method of the least squares.

Parameter (*Eq.* 8)	V^E (cm^3/mol)	G^E (J/mol)	η^E (cP)	σ^E ($dyne/cm$)
		Temp. 20.0°C		
A_0	−4.3942	647.690	−0.0969	1.8635
A_1	−0.5654	174.133	0.0004	0.0208
A_2	−0.0881	49.383	−0.0001	0.0126
SD	0.0021	0.286	0.00003	0.0019
		Temp. 30.0°C		
A_0	−4.1148	525.307	−0.1007	1.0814
A_1	−0.6061	87.558	−0.0067	0.1152
A_2	0.9951	75.860	0.0027	0.3636
SD	0.0381	5.860	0.0012	0.0169
		Temp. 40.0°C		
A_0	−3.7725	599.094	−0.0716	−1.354
A_1	−0.7483	130.337	0.000	0.486
A_2	2.2926	110.552	−0.0004	0.919
SD	0.0535	1.777	0.0002	0.027
		System 2-Butanone + *n*-Butyric acid		
		Temp. 20.0°C		
A_0	−3.5904	528.280	−0.4740	1.088
A_1	−0.3986	−42.706	−0.0001	−0.189
A_2	−0.2629	−66.261	−0.0005	0.224
SD	0.0050	0.495	0.0003	0.004
		Temp. 30°C		
A_0	−3.3316	567.985	−0.3677	−1.090
A_1	−0.2150	11.305	0.0007	−0.752
A_2	−0.1015	−20.084	0.0036	0.970
SD	0.0043	0.662	0.0001	0.023
		Temp. 40°C		
A_0	−2.6023	775.924	−0.2253	−1.576
A_1	−0.2086	146.834	−0.0002	−0.172
A_2	−0.0363	27.378	−0.0002	0.307
SD	0.0009	0.079	0.0003	0.006

$$V_{c\,mix} = x_1^2 V_{c1} + x_2^2 V_{c2} + 2x_1 x_2 [V_{c1}^{1/3} + V_{c2}^{1/3}]/8$$

$$T_{c\,mix} = \{x_1^2 T_{c1} V_{c1} + x_2^2 T_{c2} V_{c2} + 2x_1 x_2 \psi_{12} [T_{c1} V_{c1} T_{c2} V_{c2}]^{1/2}\}/V_{c\,mix}$$

η_1 to be evaluated at a temperature $T(T_{c1}/T_{c\,mix})$

η_2 to be evaluated at a temperature $T(T_{c2}/T_{c\,mix})$

T being the system temperature and ψ_{12} the interaction parameter having a value near to unity.

Various models used for testing the binary surface tension data are given below.

The Zihao and Jufu[15] model equation based on the work of Hildebrand and Scott[18] can be written as:

$$\sigma_{mix} = \frac{x_1\sigma_1}{x_1 + Ax_2} + \frac{x_2\sigma_2}{x_2 + Bx_1} \tag{14}$$

where A and B are interaction parameters.

The model of Rice & Teja[16] based on theory of corresponding states can be expressed as:

$$\sigma_{mix}/\phi_{mix} = x_1\sigma_1\phi_1 + x_2\sigma_2\phi_2 \tag{15}$$

where,

$$\phi_i = V_{ci}^{2/3}/T_{ci} \qquad \text{for } i = 1, 2 \text{ or mix}$$

$$V_{cmix} = x_1^2 V_{c1} + x_2^2 V_{c2} + 2x_1x_2[V_{c1}^{1/3} + V_{c2}^{1/3}]/8$$

$$T_{cmix} = \{x_1^2 T_{c1} V_{c1} + x_2^2 T_{c2} V_{c2} + 2x_1x_2\psi_{12}[T_{c1}V_{c1}T_{c2}V_{c2}]^{1/2}\}/V_{cmix}$$

Here σ_1 is to be evaluated at a temperature $= T(T_{c1}/T_{cmix})$ and σ_2 at a temperature $= T(T_{c2}/T_{cmix})$. The surface tension data has also been fitted to an empirical two-constant model expressed as:

$$\sigma_{mix} = x_1\sigma_1 + x_2\sigma_2 + x_1x_2[A' + B'(x_1 - x_2)] \tag{16}$$

where A' and B' are binary interaction parameters. The parameters corresponding to Eqs (9), (11)–(16) have been determined using a least squares method and are reported in Table 4. The value of ψ_{12} in eqs (13) and (15) has been assumed to be 1.05.

RESULTS AND DISCUSSION

The experimental values of physical properties of both the systems are collected in Table 2. The value of the Grunberg–Nissan parameter, d, is positive for both the systems; indicating the presence of specific interactions between the two components.[17]

The models of McAllister and Heric produce satisfactory results; while Auslander's model predicts very well the viscosity data of both the systems. The Teja and Rice

Table 4 Interaction parameters for various models and standard deviations (SD) determined by least square method.

Model	*Constants*	Temp. → 20°C	30°C	40°C
System 2-Butanone + *n*-Propionic acid				
McAllister	η_{12}	0.66580	0.57654	0.52062
(Eq. 9)	η_{21}	0.86888	0.75931	0.67341
	SD	0.00046	0.00114	0.00024
Heric	δ_{12}	0.30630	0.24370	0.25950
(Eq. 11)	δ_{21}	0.07370	0.03820	0.05620
	SD	0.00048	0.00120	0.00025
Auslander	B_{12}	0.38943	1.00878	1.09501
(Eq. 12)	A_{21}	0.34199	0.86843	0.95699
	B_{21}	2.51525	0.93723	0.89408
	SD	0.00010	0.00110	0.00001
Teja & Rice	ψ_{12}	1.05	1.05	1.05
(Eq. 13)	SD	0.00160	0.00130	0.00076
Zihao & Jufu	A	0.97456	3.24517	2.75450
(Eq. 14)	B	0.95483	0.30852	0.36350
	SD	0.00170	0.13740	0.6454
Two Parameter model	A′	1.86540	1.13340	−1.2233
(Eq. 16)	B′	0.02030	0.10090	0.4502
	SD	0.00183	0.01960	0.0391
Rice & Teja	ψ_{12}	1.05	1.05	1.05
(Eq. 15)	SD	0.445	0.444	0.564
System 2-Butanone + *n*-Butyric acid				
McAllister	η_{12}	0.71233	0.64189	0.5871
(Eq. 9)	η_{21}	1.10011	0.96222	0.8322
	SD	0.00065	0.00023	0.0002
Heric	δ_{12}	0.27270	0.28060	0.3475
(Eq. 11)	δ_{21}	−0.01140	0.00850	0.0603
	SD	0.00069	0.00024	0.0002
Auslander	B_{12}	1.44144	1.25175	1.3144
(Eq. 12)	A_{21}	1.01044	0.90231	1.0173
	B_{21}	0.56731	0.68038	0.6954
	SD	0.00001	0.00010	0.00001
Teja & Rice	ψ_{12}	1.05	1.05	1.05
(Eq. 13)	SD	0.0018	0.00308	0.0023
Zihao & Jufu	A	2.95190	1.88686	2.0408
(Eq. 14)	B	0.35655	0.53012	0.4894
	SD	0.02040	0.06730	0.5975
Two Parameter model	A′	1.12090	−0.95190	−1.5322
(Eq. 16)	B′	−0.18850	−0.74740	−0.1709
	SD	0.00841	0.03800	0.0114
Rice & Teja	ψ_{12}	1.05	1.05	1.05
(Eq. 15)	SD	0.64400	0.73700	0.7240

model, which is based on theory of corresponding states, also predicts the binary viscosity data to within reasonable accuracy for an assumed value of $\psi_{12} = 1.05$.

The surface tension data is well predicted by the proposed empirical two-parameter model (Eq. 16) compared to Rice and Teja model. The Zihao and Jufus model based on the Hildebrand–Scott equation[18], also predicts satisfactory results for the systems studied.

References

1. R. K. Wanchoo and J. Narayan *J. Phys. Chem. Liq.*, **25**, 15 (1992).
2. R. K. Wanchoo, J. Narayan, G. K. Raina and G. A. Wani, *J. Chem. Eng. Commu.* **69**, 225 (1988).
3. R. K. Wanchoo, J. Narayan, G. K. Raina and V. K. Rattan, *J. Chem. Eng. Commu.*, (1989).
4. J. Narayan, R. K. Wanchoo, G. K. Raina and G. A. Wani, *Can. J. Chem. Eng.* **66**, 1021 (1988).
5. J. A. Riddick and W. B. Bunger, *Techniques of Chemistry*, Vol-II, (Wiley–Interscience, New York, 1970).
6. B. P. Levitt, *Findlay's Practical Physical Chemistry*, Ninth Edn., (Longman, London, 1973).
7. A. Weissberger, *Techniques of Organic Chemistry*, Third Edn., Vol. VII, (Interscience, New York, 1965).
8. L. Grunberg and A. H. Nissan, *Nature* (London), **164**, 799 (1949).
9. R. C. Reid, J. M. Prausnitz and T. K. Sherwood, *The properties of Gases and Liquids*, Third Edn., (McGraw Hill Book Company, New York, 1958).
10. O. Redlich and A. T. Kister, *Ind. Eng. Chem.* **40**, 345 (1948).
11. R. L. McAllister, *AIChE J*, **6**, 427 (1960).
12. E. L. Heric, *J. Chem. Eng. Data*, **11**, 66 (1966).
13. G. Auslander, *Br. Chem. Eng.*, **9**, 610 (1964).
14. A. S. Teja and P. Rice, *Ind. Eng. Chem.* (F), **20**, 77 (1981).
15. Wang Zihao and Fu Jufu, private communication.
16. P. Rice and A. S. Teja, *J. Colloid and Interface Science*, **86**, (1) 158 (1982).
17. R. J. Fort and W. R. Moore, *Trans. Faraday Soc.*, **62**, 1112 (1966).
18. J. H. Hildebrand and R. L. Scott, *The Solubility of non-Electrolytes*, 3rd Edn., (Dover, New York, 1964).